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## Electrochemical Industry

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ADVERTISING RATES GIVEN ON APPLICATION.

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## CONCENTRATION CHANGES IN THE LEAD CELL AND IN THE OXYGEN-LIFT CELL.

In this issue we publish the first part of an article by Mr. M. U. Schoop, giving an account of an able and interesting experimental investigation of the concentration changes and diffusion phenomena in the alkaline accumulator with constant electrolyte or "oxygen-lift cell," as christened by Dr. A. E. Kennelly. Mr. Schoop's method is very simple in principle, and extremely pretty. It consists essentially in suspending the accumulator electrode to be tested on the beam of a balance and observing its changes of weight while current is flowing and after it is interrupted. If we know exactly the chemical reaction which takes place in the active material of the plates, we can easily calculate the change of weight of the active materials themselves during the passage of a certain number of ampere-hours. This calculated value will generally differ from the change of weight found experimentally by Mr. Schoop's method, for the following reasons. First, there will be in general a change of the volume and the concentration of the solution in the pores of the plate, while current is passing; secondly, the weight of the electrode in solution equals its weight in air minus the weight of the displaced solution; hence, if the concentration of the outside solution changes, or if the accumulator plate undergoes a contraction or expansion, it will manifest itself in the weighings by Mr. Schoop's method. By varying the conditions of the experiment, it is possible to analyze the different effects which cause the change of weight found by this method.

Mr. Schoop has formerly applied this method to a study of the concentration changes in the pores of the lead accumulator. In this case the concentration changes are of utmost importance. It is well known that the e. m. f. of a lead cell depends on the concentration of the acid, and if a lead cell is discharged, the formation of sulphate at both plates necessarily causes a decrease of the concentration of the acid and therefore a decrease of the e. m. f. of the cell. If the discharge is made at a very low rate, diffusion and convection will have time to annihilate any concentration differences between the solution in the pores and outside so that the concentration in the acid of the pores of the plates is essentially the same as the concentration of the outside acid between the two plates. Since we have a decrease of this total concentration proportional to the ampere-hours given out by the cell, the e. m. f. will decrease correspondingly and gradually. If, however, a lead cell is discharged at a high rate, diffusion and convection will have no time to annihilate concentration changes between the acid in the pores and the outside acid, and the concentration of the

acid in the pores will be much lower than the concentration of the outside acid. Since the seat of the e. m. f. is essentially at the contact of the active material with the liquid (that is, the liquid in the pores), the accumulator will behave practically at any moment as though the whole cell contained solution of the concentration existing in the pores of the plates. Since the latter is very low with high discharge rates, the e. m. f. will be much lower than corresponds to the concentration of the outside acid between the two plates. This is the reason of the relatively excessive voltage drop which occurs in every lead cell at high discharge rates, and that this is the only essential reason, has been conclusively proven in several ways, especially by the extended researches of Dr. F. Dolezalek. This also gives the explanation of the fact that a lead cell having been discharged at a high rate, and having undergone a considerable voltage drop will increase again in e. m. f. after the circuit is broken; for now diffusion and convection will carry the more concentrated outside acid into the pores of the plates and the e. m. f. will therefore rise until all concentration differences in the cell are annihilated. This proves that in the lead accumulator the excessive voltage drop, observed with a high discharge rate, is a necessary consequence of the electrochemical reaction which goes on during discharge. The only means by which it would be possible to diminish this voltage drop would be to increase the porosity of the active material; but there is a limit to any such attempt, since it is necessary to keep the plates in a strong condition.

Mr. Schoop has now applied his method of weighing to the study of the concentration changes in the alkaline accumulator with constant electrolyte. Mr. Schoop is particularly fitted for this investigation, not only on account of his former work with the lead cell, but for the reason that he is now developing for a German storage battery company the nickel-iron accumulator of Dr. W. Jungner who has been working along the lines of the oxygen-lift cell, independently of Mr. Edison. A study of the concentration changes is well suitable to emphasize and explain one special advantage which the Edison accumulator has over the lead cell, namely, that it is far more able to be discharged at a high rate without loss of capacity than the lead cell. We have discussed above what happens in the lead cell at a high discharge rate. What happens in the Edison cell is entirely different. The principal result of the reaction is here a transport of oxygen from one plate to the other, while the solution and its concentration between the two plates remain unchanged. There are, however, variations of concentration in the pores of the two plates, the concentration increasing in the one plate and correspondingly decreasing in the other plate. This follows from theoretical considerations and has been proven to be correct by Mr. Schoop's experiments. It also follows from theoretical considerations that the change of e. m. f., due to the increase of the concentration in the one plate and the decrease of the concentration in the other plate, will be relatively small if these changes of concentration are not very great; certainly the variation of e. m. f. due to this cause is smaller than the variation of the e. m. f. in the lead cell. For this reason, a study of the concentration changes of the Edison accumulator would appear to be more of theoretical interest

than of practical value, but as will be seen, Mr. Schoop's method enables him to use his experiments for drawing conclusions of practical importance.

Since the concentration of the KOH solution between the two plates does not change during discharge, the changes of weight of the plate which are observed by weighing the plate in the solution, can be due to the following three causes only. First, the weight of the solid active material changes on account of the oxidation of the one plate, and the reduction of the other; this change of weight can be easily calculated under the supposition that the cell is really an oxygen-lift cell. Secondly, there may be a contraction or expansion of the electrode plates; any contraction will manifest itself by an increase of weight of the plate in the solution since now a smaller volume of solution is displaced than before. Thirdly, there is a change of the concentration of the solution in the pores. This latter change of concentration can be rendered negligible by discharging the cell at a very low rate, so that the diffusion and convection have time to counteract all concentration changes. In this case, therefore, any excess of the increase of weight which may be observed beyond that accounted for by oxidation must be attributed to a contraction of the plate. In this way Mr. Schoop is enabled to study the change of the dimensions of the plate during discharge. If, however, a cell is discharged at a high rate, concentration changes will develop and will manifest themselves in a weight curve differing from that for slow discharges. That, indeed, this difference is due to the concentration changes, can be shown by observing the change of weight after the current is interrupted. Then the concentration changes will be gradually annihilated and any change of weight after interruption of the current must be attributed to this fact. The curves given by Mr. Schoop on these points are very interesting.

A study of the contraction and expansion of the electrodes of the Edison battery should give results of practical importance. We know that the concentration changes have not such an important influence on the e. m. f. curve as in the lead cell and a great part of the voltage drop observed in the Edison battery must therefore be attributed to an increase of internal resistance. This increase of internal resistance must be found inside the active materials of the plates. These active materials are contained in little perforated boxes, and when a discharge begins the layer of the active material next to the walls of the box will first be oxidized or reduced, since it is next to the outside liquid. When the discharge continues the places of oxidation and reduction will be gradually removed inwards towards the center of the boxes. The current then has to pass from the outside solution through the perforations in the boxes, through the liquid in the pores to those particles of active material in the center which are to be oxidized or reduced at that moment. From these particles, the current then must go back again to the metallic walls of the boxes, since the latter are connected to the terminals of the cell. The change of internal resistance in the plates of the Edison accumulator will, therefore, be partly due to a change of the resistance of the liquid in the pores (due to the change of its configuration and its

concentration) and partly to a change of the resistance of the solid particles through which the current passes from the places of oxidation and reduction to the outside walls of the boxes. These solid particles are a mixture of the active iron or nickel materials with some material of high conductivity, like graphite. For this reason the addition of graphite or the like to the active materials and the pressure under which they exist are of great importance for the internal resistance, and therefore for the whole behavior of the Edison cell. In looking over Mr. Edison's patents, one will find that Mr. Edison early recognized the importance of these facts and studied the best conditions of preparing this mixture very thoroughly and extensively. Now, of course, any expansion or contraction of the plates will have a great influence on their internal resistance, and for this reason the application of Mr. Schoop's method should lead to results of practical importance.

#### MOVING ELECTRODES.

While there is nothing novel in the method of changing the position of an electrode in electrolytic as well as electric furnace work for the purpose of regulating the current during operation, yet the gradual raising of an electrode has recently been made use of for a new and peculiar purpose, namely, for building up the product of an electrochemical reaction in a certain desired shape. In this issue we publish some information on two processes of this kind. Prof. Elihu Thomson has patented such a method for making hollow silica tubes in what is essentially a miniature electric arc furnace. He places pulverized quartz around two vertical carbon rods of suitable cross-section which form the electrodes, and by slowly raising the upper electrode, he draws a gradually lengthening arc and thereby produces a progressive fusion of the layer of quartz next to the electrode surface. In a German Bunsen Society paper Dr. Rathenau describes a method of making calcium sticks or rods by raising the cathode gradually during electrolysis in such a way that the calcium deposited at the end of the cathode always remains just in contact with the fused bath.

#### ELECTROMETALLURGY OF IRON AND STEEL.

In this issue we publish an abstract of the very interesting report made by the commission which was appointed by the Canadian Government to study the more prominent electric iron and steel furnace processes in Europe. The report contains some very interesting details concerning the plants visited by the commission, but its chief interest should lie in the very favorable conclusion reached by the commission on the possibilities of electric furnace processes in the reduction of iron ores. The cost given for the Keller process is surprisingly small; however, in this estimate the cost of one electric horsepower-year is taken at \$10.00, which is an extremely low figure. Moreover it is well to keep in mind that the conclusions reached by the commission refer to the industrial conditions of Canada and that the local conditions in Canada, where good iron ores and water powers are plentiful and fuel is scarce, are much more favorable to electric iron and steel processes than for instance, in the Pittsburg district. Nevertheless, the metallurgical world will certainly watch with the greatest interest the developments in Canada.

In connection with this matter, it may not be out of place to refer briefly to the various ways in which electrical energy may be utilized in the iron and steel industries, besides the application for power purposes. In speaking of electric iron and steel processes, most people think only of the reduction of iron ores. True, this is the biggest problem, and various attempts have been made to solve it on a somewhat large experimental scale, although no process of this kind has yet proven successful on a commercial stage. The developments in Canada give new interest to this problem. But there are many other smaller, yet important problems, in which the iron and steel metallurgist could make use of the electric current which is now already available in every modern plant for lighting and power. The use of electric current for magnetic separation of lean ores is well known; electrostatic separation is being tried. The electrolytic refining process of Messrs. Burgess and Hambuechen enables us to get really pure iron if we want it. Mr. Edison is able to make seamless steel containers for his storage battery by electrolytic deposition.

On the other hand, electric furnace processes are in use on a commercial scale at various places for making ferro-alloys; if the starting material is a mixture of scrap iron with the oxides of the elements to be alloyed, like titanium, silicon, etc., the electric furnace has proven superior to the old methods, since it easily gives the extremely high temperature required for the reduction. For the preparation of special steels, various electric furnace processes have proven extremely useful on account of the ease of control, the cleanliness of operation and the absolute freedom from fuel gases. The only problem to be solved here by the electrometallurgical designer is to prevent any impurities coming into the fused metal bath from the electrodes, if electrodes are used. We have repeatedly referred to the ingenious methods by which this problem has been solved in different ways by Messrs. Kjellin, Heroult and Gin. First-class steels are now made in electric refining furnaces on a commercial scale, and they are able to compete successfully with the best grades of crucible steel. As Mr. Bennie remarked in a recent paper before the Foundrymen's Association, electrometallurgists are undoubtedly hitting the older art at the weakest spot when attacking it from the crucible steel standpoint. Finally, it may be found quite practical to use electric furnace methods in connection with our ordinary non-electrical metallurgical furnaces for special purposes, if a high heat is required at a certain moment and at a certain point. To such purposes the electric method is admirably adapted. Thus the suggestion was made by Dr. Richards in his recent presidential address to the American Electrochemical Society that it is a distinct commercial possibility to use electric heating to take off the peak of the load in our open-hearth steel furnaces, *i. e.*, to furnish electrically the last few hundred degrees of necessary temperature, while the combustion of gas furnishes the lower range. Mr. C. P. E. Schneider's patent, abstracted in this issue, is also quite suggestive in connection with this problem. It will thus be seen that the prospects of electric furnace methods in the iron and steel industries are very good in a great many different directions. But future advances will essentially rest on the judicious use of the principles of electric heating, *i. e.*, on furnace design, based on exact scientific principles and on experience.



## INTERNATIONAL ELECTRICAL CONGRESS.

We are informed that the acceptances of membership in the International Electrical Congress of September 12-17, in St. Louis, number 1762, and that over 160 specially invited papers are promised, in all. One thousand certificates of membership have been issued to those who have become members by sending in their subscription, and about 100 more certificates are about to be issued.

Efforts are being made to secure the manuscripts of as many of the 160 papers as possible, by the first of July, in order to have them printed in advance and distributed among the Congress members at St. Louis. Thus far, six papers have been delivered, and many more are promised by that date.

The programmes scheduled for Sections D and E are here given. The similar programmes of Sections A, B and C have already been published in our June issue, page 214.

All communications concerning the congress should be addressed to the General Secretary, Dr. A. E. Kennelly, Harvard University, Cambridge, Mass.

## SECTION D.—ELECTRIC POWER TRANSMISSION

The chairman of the section is Mr. Charles F. Scott; the secretary, Dr. Louis Bell. The following papers have been promised:

E. Bignami, "Electrical Transmission Plants in Switzerland."

H. M. Hobart, "Conditions Conducive to Economy in Motor Design."

Maurice Leblanc, "Transmission of Alternating Currents Over Lines Possessing Capacity."

G. Mengarini, "Utilization of Hydraulic Powers in Italy."

F. G. Baum, "High-Potential Long-Distance Transmission and Control."

D. O. Blackwell, "The Tower-System of Line Construction."

H. W. Buck, "The Use of Aluminium as an Electrical Conductor."

V. G. Converse, "High-Tension Insulators."

M. H. Gerry, Jr., "Line Construction and Insulation for High Tensions."

L. M. Hancock, "Bay Counties Transmission System."

R. L. Hayward, "Some Practical Experiences in the Operation of Many Power Houses in Parallel."

J. F. Kelly and A. C. Bunker, "Long-Distance Power Transmission."

P. M. Lincoln, "Transmission and Distribution Problems Peculiar to the Single-Phase Railway System."

R. D. Mershon, "The Maximum Distance to Which Power can be Economically Transmitted."

P. N. Nunn, "Pioneer Work of the Telluride Power Company."

J. S. Peck, "The High-Tension Transformer in Long-Distance Power Transmission."

F. A. C. Perrine, "American Practice in High Tension."

C. P. Steinmetz, "Theory of Single-Phase Motors."

## SECTION E.—ELECTRIC LIGHT AND DISTRIBUTION.

The chairman of this section is Mr. J. W. Lieb, Jr., the secretary, Mr. Gano S. Dunn. The following papers have been promised:

André Blondel, "Impregnated Arc-Light Carbons."

Max Déri, "Single-Phase Motors."

E. de Fodor, "Rates for Electricity Supply."

E. Jona, "Insulating Materials in High-Tension Cables."

W. Kübler, "Upon Means for Compensating the Series-Connection of Induction Motors."

Karl Roderbourg, "Storage Batteries."

Guido Semenza, "Commercial Limits of Electric Transmission, with Special Reference to Lighting Service."

G. Stern, "The Superiority of the Alternating Current for Distribution in Large Cities."

W. Wedding, "Measurements of the Energy of Light and Heat Radiation from Electric Light Sources."

Arthur Wright, "Recent Improvements in Electrolytic Meters."

S. P. Thompson, Subject to be Announced.

B. H. Behrend, "The Testing of Alternating-Current Generators."

George Eastman, "Protection and Control of Large High-Tension Distribution Systems."

W. C. L. Eglin, "Rotary Converters and Motor Generators in Connection with the Transformation of High-Tension Alternating Current, to Low-Tension Street Current."

W. L. R. Emmet, "The Effect of Steam Turbines on Central Station Practice."

Louis A. Ferguson, "Underground Electrical Construction."

Gerhard Goettling, "Storage Batteries as an Adjunct to Central Station Equipment."

G. Ross Green, "American Meter Practice."

Caryl D. Haskins, "Metering Efficiency on Customers' Premises."

Francis Hodgkinson, "Steam Turbines."

John W. Howell, "Incandescent Lamps."

Philip Torchio, "Distributing Systems from the Standpoint of Theory and Practice."

W. F. White, "The Selection of a Distributing System for a Large City."

The following bodies have already promised to hold simultaneous conventions and joint sessions: The American Institute of Electrical Engineers, the American Electrochemical Society, the American Physical Society, the International Association of Municipal Electricians, the American Electrotherapeutic Association.

The following bodies have promised to send delegates to the Congress: The National Electric Light Association, The Association of Edison Illuminating Companies, the Société Internationale des Electriciens, Der Schweizerische Elektrotechnische Verein.

The delegates accredited to the Congress from various co-operating bodies are not expected to be called upon to vote upon any questions of international importance. All matters concerning units, standards, etc., will lie within the province of the Chamber of Government Delegates.

The delegates of the American Institute of Electrical Engineers and their papers to the Congress are as follows: Ralph D. Mershon, Section D., "The Maximum Distance to which Power can be Economically Transmitted;" M. I. Pupin, Section A., "Electrical Impulses and Multiple Oscillators;" C. P. Steinmetz, Section D., "The Theory of the Single-Phase Motor."

The delegates of the American Electrochemical Society and their papers to the Congress are as follows: W. D. Bancroft, Section C., "The Chemistry of Electroplating;" H. S. Carhart (with Dr. G. A. Hulett), Section C., "The Preparation of Materials for Standard Cells and their Construction;" L. Kahlenberg, Section C., "The Electrochemical Series of the Metals."

The delegates of the National Electric Light Association and their papers to the Congress are as follows: George Eastman, Section E., "Protection and Control of Large High-Tension Distributing Systems;" G. Ross Green, Section E., "American Meter Practice;" F. A. C. Perrine, Section D., "American Practice in High-Tension Line Construction and Operation."

The delegates of the Association of Edison Illuminating Companies and their papers to the Congress are as follows: W. C. L. Eglin, Section E., "Rotary Converters and Motor Generators in Connection with Transformation of High-Tension Alternating Current to Low-Tension Direct Current;" L. A. Ferguson, Section E., "Underground Electrical Construction;" Gerhard Goettling, Section E., "Storage Batteries as an Adjunct to Station Equipment."



## SOME NOTES ON PLATINUM AND ITS DETERIORATION.

BY WILLIAM CAMPBELL, PH. D.

The great importance of platinum in the determination of high temperatures and other uses makes it one of the most interesting of metals. Its liability to deteriorate is well known to all, though the cause for such deterioration is not always apparent. The following notes on its crystalline structure, its occlusion of and permeation by gases, its behavior at high temperatures, etc., will therefore not be out of place.

## CRYSTALLINE STRUCTURE.

When the surfaces of buttons of platinum are examined, large dendritic crystals are often seen. These dendrites consist of two axes at right-angles, which form the skeleton or framework of the grains or crystals, as in the case of most other metals. Andrews<sup>1</sup> has examined the microcrystalline structure of platinum. A small ingot was used and etching was performed by means of boiling aqua regia. Under a magnification of 360 diameters, primary and secondary crystals are seen (cp. those of lead, iron, etc.). The size of the primaries varied from 0.002 to 0.04 inch, and that of the secondaries from 0.0002 to 0.007 inch. Andrews states that the crystalline structure of platinum appears to generally resemble that of gold and silver. The effects of stress on platinum were also studied.<sup>2</sup> A cube of platinum 0.30 inch square was carefully polished and a force producing a compression of 10 per cent on the total height of the cube was applied. Upon examination it was found that innumerable fine "slip-bands" had been produced in many of the primary grains or crystals. As in the case of other metals it was found that stress alone, without etching, will often reveal the boundaries of the large grains or primary crystals. The finer "slip-bands" apparently show the crystalline slip which occurs along the facets of the smaller secondary grains.

## DIFFUSION AND OCCLUSION OF GASES.

Sainte Claire-Deville and Troost discovered that hydrogen would pass through a plate of platinum prepared from the fused metal or through iron, at a red heat.<sup>3</sup> Graham's work along this line is well known.

The occlusion of oxygen and hydrogen by platinum black has been studied by Mond, Ramsay and Shields.<sup>4</sup> The results of Graham were confirmed by experiments with platinum sponge and foil. Platinum black, after drying at 100° C., is found to contain 0.5 per cent H<sub>2</sub>O, which can be removed in a vacuum at 400° C., when platinum black is converted into a sponge. At any given temperature the water retained by platinum black is constant. The density of platinum black, dried at 100° C., is 19.4, and allowing for water retained by it, is 21.5. Platinum black contains 100 volumes of oxygen, which begins to come off in quantity at 300° C. in vacuo, while the bulk has been given off at 400° C. A red heat is necessary for complete removal. Small quantities of CO extracted between 100° and 200° C.

About 310 volumes of hydrogen are absorbed, of which 200 volumes are converted into water and only 110 are really occluded. Part can be removed at normal temperature in vacuo, but the larger portion comes off at 250° to 300° C., while a red heat is necessary for complete removal. They conclude that there is not sufficient evidence for Pt<sub>2</sub>H<sub>2</sub> and Pt<sub>3</sub>H<sub>2</sub>, and the arguments put forward by Berthelot are not justified. They consider that the heats of combination determined by Berthelot and Favre are valueless. The heat measured was due to the formation of water. In the case of Palladium<sup>5</sup>, they find that there is no compound formed.

A. de Hemptinne, writing on the catalytic action of platinum

black<sup>6</sup>, describes the occlusion at very low temperatures. The absorption of hydrogen by carbon is mechanical, and at -78° C. is far greater than at +15°. In the case of platinum, however, the reverse holds good, and in all the experiments he finds the absorption to be greater the higher the temperature. If the absorption tube be allowed to return to the higher temperature slowly, at about -40° C. a marked absorption of gas occurs. His experiments lead him to believe that a compound of hydrogen and platinum is indicated.

Harbeck and Lunge<sup>7</sup> have studied the action of carbonic oxide on platinum and palladium. They find that platinum black absorbs sixty times its volume of CO, while palladium absorbs thirty-six times its volume. A true chemical compound is probably formed, since the subsequent action of other gases, as hydrogen, does not eliminate the CO. It is very stable, but at 250° C. it suddenly decomposes into its constituents. As yet it has not been isolated.

The permeation of hot platinum by gases was observed by Randall<sup>8</sup>, who found that hot platinum was permeated by hydrogen, but not so rapidly as Graham would lead one to believe. It is not permeated by either of the constituents of air nor by methane in spite of the latter's low density.

Winkelmann<sup>9</sup> points out that the rate of diffusion of hydrogen increases after the platinum has been heated for some time. This is due to the crystalline structure assumed by the metal and not to the expulsion of occluded air. He further states that the diffusion of hydrogen through red-hot platinum is not proportional to the pressure of the gas; it seems probable that the diffusion is accompanied by a dissociation of the molecules, and that only atoms of hydrogen pass through the metal.

PLATINUM ELECTRICAL-RESISTANCE PYROMETERS.<sup>10</sup>

Many years ago Matthiessen pointed out that the resistance of a wire of almost any pure metal increased nearly in proportion to the absolute temperature. Between 0° and 100° C. the increase in resistance of pure platinum wire is nearly 34 per cent, while at 1000° C. the resistance is approximately four times that at 0° C.

To Siemens is due the credit of working out the platinum resistance pyrometer in practical form and introducing it into use. The theory of the method and description of instruments for the measurement of temperatures up to 1000° C. were embodied in his Bakerian Lecture in 1871. In 1874 a report to the British Association condemned the method. This was based on experiments carried on in an ordinary open fire at about 800° C. The resistance was found to increase continuously with continued heating, and the wire to become rapidly deteriorated. There was a continuous change of zero. However, Callendar<sup>11</sup> showed that even at high temperatures the pyrometers could be made practically free from change of zero provided the wire was properly protected from strain and from contamination.

The sensitive part of the instrument is the coil of platinum wire, which is wound on a clay cylinder and placed in an iron tube about an inch in diameter and 5 feet or more long. Callendar examined an instrument (used at the Woolwich Arsenal) whose resistance had increased some 15 per cent, though never heated above 900° C. He found that the wire in places was brittle and stuck to the clay cylinder. He judged from the local nature of the action that the wire had been attacked by the clay or some impurity in it. He has found that mica is the best insulator, for it has no action on the wire, even at 1200° C. Platinum wire is readily attacked by metallic vapors. In the case of a pyrometer with copper electrodes which had been heated to about 850° C. for an hour in

<sup>1</sup> Proc. Royal Society, London, vol. 69, p. 433; Metallographist V, p. 233.

<sup>2</sup> Proc. Royal Society, London, vol. 70; Metallographist V, p. 236.

<sup>3</sup> Roberts-Austen: An Introduction to Metallurgy (1898), p. 54.

<sup>4</sup> Proc. Royal Society, London, 1895, 58, p. 242; 1897, 62, p. 50.

<sup>5</sup> Proc. Royal Soc., London, 1897, 62, p. 290.

<sup>6</sup> Zeits. Physik. Chem., 1898, 27, p. 429; Abst. J. Chem. Soc., London, 1899, II, p. 146.

<sup>7</sup> Zeits. Anorg. Chem., 1898, 16, p. 50; Abst. J. Chem. Soc., 1898, II, p. 106.

<sup>8</sup> Amer. Chem. Journal, 1897, 19, p. 682.

<sup>9</sup> Ann. Physik., 1902 (IV), 8, 338; Abst. J. Chem. Soc., 1902, II, p. 552.

<sup>10</sup> H. L. Callendar: Journal Iron and Steel Inst., 1892, I, p. 164.

<sup>11</sup> Phil. Trans. Royal Society, 1887, p. 161.

a porcelain tube, the marked discoloration of the mica near the copper leads showed that copper is appreciably volatile at that temperature. Owing to the action of the copper the resistance of the platinum coil showed an increase of nearly  $\frac{1}{2}$  per cent. For the above reason copper or silver leads ought not to be used for high temperature work. Again, solder of any kind cannot be used. Porcelain tubes will be found to give the best protection to the wire.

#### THERMO-ELECTRIC PYROMETERS.<sup>13</sup>

Becquerel was the first to use the discovery of Seebeck to measure high temperatures, and he used a platinum palladium couple. Pouillet studied the method and compared an iron platinum couple with an air thermometer. Later Ed. Becquerel took up the study of the platinum palladium couple of his father, and was the first to see the necessity for using a high resistance galvanometer in order that the change in resistance of the couple on heating might be negligible when compared with the total resistance of the circuit. Regnault

important source of error is due to annealing, because, on heating a wire at a point between the hardened and the annealed part, a current is developed whose strength depends upon the kind of wire and the degree of hardness. All wires ought therefore to be carefully annealed. It is further pointed out that platinum and its alloys are liable to change, and on heating for a certain length of time, especially between the temperatures of 1000° and 1200° C. become brittle. This change is due to crystallization, and is more rapid in the platinum-iridium alloy than in that of platinum-rhodium, while in pure platinum the change takes place more slowly than in either. The greatest alteration is caused by a reducing atmosphere, and in a fire-clay furnace platinum wires are slowly destroyed.

#### DISINTEGRATION OF THE PLATINUM METALS IN DIFFERENT GASES

Holborn and Wien<sup>14</sup> in a comparison between the methods of measurements of high temperatures (electric-resistance and

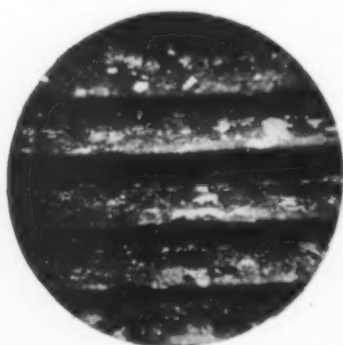


FIG. 1.—PLATINUM WIRE  $\times 35.0$ .



FIG. 2.—PLATINUM WIRE  $\times 35.0$ .



FIG. 3.—PLATINUM WIRE  $\times 35.0$ .



FIG. 4.—PLATINUM WIRE  $\times 35.0$ .



FIG. 5.—PLATINUM + 10 % Rh.  
WIRE  $\times 35.0$ .



FIG. 6.—PLATINUM + 10 % Rh.  $\times 35.0$ .

used and condemned Pouillet's couple on account of the irregularities he met with, but as he does not seem to have considered a high-resistance galvanometer necessary his experiments are hardly conclusive. Le Chatelier made a thorough investigation of the thermo-electric method about the same time as Barus<sup>15</sup>, and we now have the thermo-electric pyrometer bearing his name. He found that iron, nickel, palladium and their alloys cannot be used for high temperature work, because they give rise to parasitic currents, which may sometimes be relatively intense when heated in certain of their points. Owing to the phenomena of hydrogenation the nature of palladium is completely changed and simple heating of an initially homogenous metal may cause the formation of couples. Platinum and its alloys with iridium and rhodium are free from these faults, and the irregularities previously observed are owing to the use of iron and palladium. A less

thermo-electric) soon found that above 1200° C. platinum begins to suffer from volatilization, which is strong enough to appreciably increase the resistance in the case of very fine wires. About 850° C. platinum is rapidly altered by hydrogen in the presence of siliceous material. In the case of one wire heated in an earthenware tube in an atmosphere of hydrogen, a brittleness was produced which may be accounted for by silicification of the platinum, because on heating a wire by the electric current inside a cold glass tube, even in hydrogen, no brittleness was obtained. In the case of palladium the resistance is increased some 60 per cent by the absorption of hydrogen at low temperatures, producing the hydride. If palladium is heated in an atmosphere of hydrogen in the presence of silicon, the same alteration as platinum is observed. The experiments with rhodium and iridium show that several heatings to a high temperature are necessary before they take

<sup>13</sup> La Chatelier and Boudouard: High Temp. Measurements.  
<sup>15</sup> Bull. 54, 163, U. S. Geo. Survey, etc.

<sup>14</sup> Ann. der Phys. u. Chem., 47 (1892), p. 107; 56 (1896), p. 360. Review by R. Masse: Bull. de la Soc. d'Enc., fifth ser., I. (1896), p. 1012. See also "High Temperature Measurements."

their normal resistance. Holborn and Henning<sup>18</sup> found that when heated electrically in air, the disintegration increased very rapidly with increasing temperatures. At 1670° C., platinum and rhodium showed about the same loss in weight, while iridium lost approximately ten times as much. There was no decrease in disintegration of the pure metals during the longest heating (3 hours), the loss being proportional to the time. In the case of the platinum-iridium alloys, however, changes were observed, produced no doubt by the more rapid disintegration of the iridium which caused a change of composition at the surface. Holborn and Austin<sup>19</sup> experimented with atmospheres of different gases and at different pressures. They found that the disintegration of platinum and rhodium was very similar. At atmospheric pressure, it is five times as great in oxygen as in air. In air at 25 mm. it is about  $\frac{1}{2}$  as much as at 760 mm. and in nitrogen it becomes very small. Iridium disintegrates ten times more rapidly in air than does platinum. At 25 mm. the loss is one-eighth that at 760 mm., and in oxygen the loss is eleven times as great. The phenomena are entirely different in the case of palladium. The disintegration in air increases with decreasing pressure, while the nature of the surrounding gas seemed to be without influence. When hydrogen was used, the palladium absorbed the gas and melting occurred before the temperature was reached where disintegration commences. When heated in a hydrogen vacuum, platinum and iridium showed no disintegration. Their paper is accompanied by a table of the results they obtained.

An example of the deterioration of a platinum/platinum 10 per cent rhodium thermo-couple was recently met with in some experiments on annealing of steel. The heatings were conducted in a cylindrical gas furnace, and were performed in from two to three hours. The bars of steel were packed in an iron tube with lime and asbestos, the thermo-couple being placed in the center. The wires were insulated by Morgan fire-clay tubes, surrounded by a larger porcelain tube, which, however, was open at both ends. On heating, it was noticed that a certain amount of steam issued at the beginning of the operation, which was later followed by gas leaving a black discoloration on the fire-clay tube projecting from the furnace. This gas undoubtedly arose from carbonaceous impurities in the asbestos used.

The thermo-couple did not show any deterioration or brittleness, and gave constant readings in calibration when used at medium temperatures, but above about 1050° C., it suddenly became brittle and showed a change when recalibrated, the deflections of the galvanometer giving a new, but similar curve. Under the microscope the change in structure was marked and was of two kinds. The one, evidently due to recrystallization alone, occurring within the fire-clay tubes, and the other, found in that part of the wires between the junctions of the fire-clay tubes, probably due to the evolution of gas giving rise to a rough incrustation surface to the wires. The effects were much more marked in the case of the platinum wire, while the platinum rhodium lead showed less change of structure, but was far more brittle.

Fig. 1, magnified thirty-five diameters, and obliquely illuminated, shows the structure of the platinum wire within the fire-clay tube. It is unetched, of course. Numerous large grains or crystals are seen to have grown in each of the five pieces of wire. Fig. 2, same magnification, shows even larger crystals which would well account for the brittleness of the wire.

Fig. 3 is a view of pieces of the platinum wire taken from near the ends of the fire-clay tubes, while in Fig. 4 are seen samples of the wire from between the tubes. The curious incrustation of metal almost completely hides the crystallization, and has caused a great thickening of the wire. It has been apparently caused by the evolution of gas from the metal,

for it would seem to be too coarse to be due to volatilization of the metal alone.

Fig. 5 shows several pieces of the platinum-rhodium wire from within the fire-clay tube, but the structure is not nearly so coarse as in the case of the pure platinum. Fig. 6 shows three pieces of the platinum-rhodium wire occurring between the joints of the fire-clay tubes. The incrustation is well shown, but again the structure is not nearly so coarse as in the case of the pure metal. In similar heatings, made without the packing of lime and asbestos, no such marked deterioration of the couple was noticed. From the above will be seen the necessity of enclosing the thermo-couple in a porcelain tube, to which the products evolved during heating to 1000° C. and above cannot gain admission.

To sum up, the authorities seem to agree that platinum and its alloys are more or less volatile at high temperatures; that heating to temperatures above 1000° C. for any length of time causes brittleness. Whether this brittleness is due to crystallization alone, to the formation of compounds or to the absorption and evolution of gases, has not been definitely decided. It will probably be found that the first and last are the main causes and often occur together. It is, however, generally agreed that a reducing atmosphere in the presence of siliceous material causes the greatest alteration.

### THE ELECTROLYTIC PROCESS OF REFINING GOLD ALLOYS.

By EMIL WOHLWILL, PH. D.

In an article published in the June issue of this journal, I have discussed the electrolytic process of gold refining as a satisfactory method for winning pure gold, platinum and other platinum metals from a material which is itself the product of a previous parting operation. The application of the electrolytic process is, however, not necessarily restricted to such a supplementary second parting operation. For the essential characteristic feature of the electrolytic process is to dissolve electrochemically the constituents of a material, rich in gold, in a chloride solution and to deposit afterwards chemically pure gold from the electrolyte whatever the mixture of ions in the same may be.

The electrolytic process may, therefore, be applied to directly and primarily part gold alloys, if their composition is such that when used as anodes, the different components are continuously dissolved in the electrolyte; this means that either all constituents must be dissolved under the influence of the current or the formation of certain insoluble compounds must not cause any interruption in the solution of the other constituents, even at a high current density. Wherever these conditions are fulfilled, the electrolytic process of parting gold is able to compete with the methods which are generally used for parting gold containing silver. This does not mean that the electrolytic method can claim to replace these methods under all circumstances.

As to the most generally applied method of this kind—the parting process with the aid of sulphuric acid—it may be said that its most important peculiarity is its extraordinarily manifold applicability. It is essentially the same process by which, with the aid of sulphuric acid, the smallest quantities of gold are recovered from silver poor in gold, and by which mixtures of gold and silver in any proportion (after addition of silver) can be subjected to the parting operation. If it is of prime importance to treat very different materials by the same method, a satisfactory substitute will not be easily found for the method introduced by D'Arcet.

But this applicability to manifold purposes is not of decisive importance for industrial work. This is proven by the fact that for treating silver containing gold, the sulphuric acid process has been nearly completely replaced in the United States by the electrolytic process of parting, although the method introduced by Bernhard Moebius, is so far applicable

<sup>18</sup> Sitz. Ber. der Berl. Akad. (1902), p. 933.

<sup>19</sup> Phil. Mag., sixth series, No. 40, April, 1904, vol. 7, p. 388; also Sitz. Ber. der Berl. Akad., p. 245 (1903).



only for silver containing a low amount of gold and copper. The simple reason for the preference of the electrolytic method is that for parting the immense quantities of silver which contain a low proportion of gold, the manifold applicability of the sulphuric acid process is of no value, while the Moebius process has certain great advantages which the older method lacks.

The same may be said concerning the electrolytic treatment of gold containing silver, whenever the average composition of the same permits the direct application of electrolysis and the existing conditions offer difficulties for the operation of the sulphuric acid process. Such a difficulty is in many cases the requirement of keeping in store a greater stock of metallic silver which is not always available, and the necessity of continually recovering this silver as well as a part of the consumed acid; for this purpose much space is required with the usual method. In some districts it is especially the high price of the required large quantity of sulphuric acid which renders the application difficult for the gold producer. In more civilized districts and countries, the vapors of sulphuric acid and sulphurous acid which are developed in abundant quantities, and which are considered as a great nuisance by residents in the neighborhood, may cause the superintendent of the plant to look for a process which is less obnoxious to the neighborhood.

Moreover, the sulphuric acid process never yields a complete purification of the gold, and completely excludes the parting of platinum and if platinum is present in a large proportion, the process does not yield a complete recovery of silver. The process, therefore, requires in numerous cases the use of supplementary and even complicated operations, in order to yield a product which satisfies the practical requirements of purity.

The electrolytic process avoids all these difficulties and disadvantages. It permits the treatment of a given material without any supplementary methods, hence without complications. It requires small space. Of chemical reagents, only a minimum quantity is necessary. No obnoxious vapors are developed. The product of the main operation is always pure gold, even if very complicated mixtures are treated. There is no difficulty whatever, due to platinum and iridium being contained in the gold.

As we remarked before, these advantages of the electrolytic process can be utilized only if the anodic gold is of such composition that it does not contain too much of such constituents which can prevent the continuity of the dissolution of the anode. It should not contain especially too much silver and lead. It is therefore of importance to make it absolutely clear in which proportions these elements are permitted to exist in the gold anode. Dr. Tuttle states that in the United States Mint in Philadelphia, the application of the process is limited to bullion having a fineness of not less than 0.940 gold. One might think that this figure represents the essential limitation of the process so that a content of more than 6 per cent of silver, plus lead, would make the application of the process impossible.<sup>1</sup> This figure, however, does not represent the essential limitation of the process; it is rather a consequence of the peculiar modification in which the process is used, according to Dr. Tuttle, in Philadelphia. The feature of this modification is that the baths are heated to 50° or 55° C. only. If such a low temperature is used, the gold is obtained at the cathode in the condition described by Dr. Tuttle, *i. e.*, in spongy form, so that it must be pressed or melted in order to get perfect coherence. If at a temperature of 50° to 55° C. the current density is increased beyond a certain limit, the lack of coherence of the gold becomes worse; the danger arises that a part of the precipitated gold drops off and is mixed with the anode slime. For this purpose it is necessary to use a low current density.

If, however, the electrolyte is heated to 65° or 70° C., and the amount of gold contained in the electrolyte is sufficiently

high, no soft or spongy gold is obtained, but the gold is perfectly solid. Without changing the surface of the cathode, it is possible to increase the strength of the current, and, therefore, to increase also the current density, up to the double of what is permitted at 50° to 55°, there being no danger whatever of any loss due to gold falling off.

Of equal importance is the increased temperature for the anodic reaction. The current density at which a development of gaseous chlorine starts at the anode (so that the dissolution of the anode plate is no longer complete) may be called the "density limit." Now experience shows that this density limit at the anode is the lower, the lower the temperature. The presence of a certain proportion of silver in the anode causes the latter to be covered with insoluble silver chloride, and this means a decrease of the active surface of the anode; if the current strength is maintained constant, the anodic current density is then increased. It will therefore be seen that the proportion of silver in the anode may be the greater the higher the density limit, and therefore the greater, the higher the temperature of the electrolyte.

Nevertheless, even at a temperature of 65° to 70° C., which I have given as the normal temperature of the electrolytic process in my patent specifications, the permitted proportion of silver in the anodic gold is relatively low as long as the employed current density is high, and as long as the operation is so conducted that the chloride of silver formed at the anode has so little adherence that it falls off, of its own accord, into the slime. However, even with a high current density the limitations of the process are very essentially reduced, if, with slight modifications of the apparatus and by following simple rules of precaution, the chloride of silver is scraped off from the anode plates at periodic intervals. In this way it is easy to recover directly as chemically pure gold the greatest part of the gold contained in alloys with 15 per cent of silver. It is evident that gold much richer in silver can be treated, if a stock of purer gold is available with which the alloy rich in silver can be blended so as to give an alloy containing 15 per cent of silver. In order to treat by electrolysis, for example, Klondike gold of the highest silver content given by Dr. Tuttle (0.219), it is only necessary to melt such gold with half the quantity of purer gold containing about 1 per cent of silver, as obtained from the slimes of the Moebius process or by refining with sulphuric acid. The limit of the content of silver given above is only a relative one; it relates to an operation in which it is important to recover within twenty-four hours the greatest part of the anodic gold. If this is not so important, it is possible to decrease the current with the same surface of the anodes and the proportion of silver in the gold may then be correspondingly greater.

I wish to remark that lead and bismuth contained in the anode are obnoxious to the electrolytic treatment, in so far as the allowable content of silver is reduced by about as many per cent as lead and bismuth are contained in the alloy.

If, as in the last cases, gold electrolysis is applied to alloys of gold with other metals, the continuation of the operation depends upon the requirement that gold, which has been dissolved chemically, is continuously added to the electrolyte. The reason for this is that by the electrolytic decomposition of the electrolyte, the quantity of gold deposited on the cathode corresponds to the ampere-hours passed through the electrolyte; on the other hand, the quantity of gold which is thus removed from the electrolyte is only partially replaced by the dissolution of gold from the anode, since the latter contains, besides gold, other constituents which are partly dissolved and partly changed into insoluble chlorides or sulphates. The electrolyte therefore tends to get poorer in gold and this will take place the more quickly the greater the difference between the amount of gold precipitated on the cathode and the amount of gold dissolved from the anode. The latter amount will be the smaller, the more other constituents of the anode are either dissolved or changed to insoluble chlorides in the same

time. To maintain the amount of gold in the electrolyte constant, it is necessary to add continuously new gold dissolved by a chemical operation. It is quite evident that it is advantageous to use, for this purpose, not pure gold, but the necessary amount of the same gold alloy which is under treatment. From this the advantage results that this portion is refined simultaneously with that serving as anode material. The complete content of gold of the alloy which is chemically dissolved will be precipitated by the electric current in the same chemical purity, and in the same coherent condition as the gold which passes into the solution from the anode.

There is also an economical advantage in this combination of the electric precipitation of gold which was chemically dissolved, together with the gold which had been dissolved by electrochemical action from the anode consisting of the same alloy; this advantage is that the precipitation does not require any chemical reagents, and only a small amount of electrical energy.

I will give a few figures to show the degree to which chemical work is required for this combination treatment. If a raw material is to be treated which consists of 85 per cent of gold and 15 per cent of silver, the rational operation of the process requires the chemical dissolution of 11.5 kg. of the same material for 100 kg. of gold deposited electrically; it is therefore necessary to dissolve one-tenth of the raw material in aqua regia. If, besides the 15 per cent of silver, the alloy also contains 2 per cent of copper, then the portion of the raw material to be chemically dissolved increases to 14.5 per cent; i. e., one-seventh of the total quantity.

If the problem is to win by electrolysis pure gold from alloys of the composition of modern gold coins, which are a mixture of 90 per cent gold and 10 per cent copper, then it is necessary to dissolve 20 kg. of every hundred kg. of this alloy in aqua regia and add it to the electrolyte in order to maintain constant the original amount of gold in the solution during operation up to the finish.

I have given this calculation of the treatment of gold rich in copper only as an example. It may be permitted to add a few words concerning the practical operation of such a process. In such a case copper is dissolved from the anode, but is not precipitated from the electrolyte as long as there is sufficient gold in the electrolyte; it therefore accumulates in the solution. The same may be said concerning the copper originating from the gold which is dissolved chemically and added to the electrolyte. If 100 kg. of gold containing 2 per cent of copper are treated, 2 kg. of copper will be contained in the electrolyte besides the gold; if 100 kg. of gold containing 10 per cent of copper are treated, 10 kg. of copper will be contained besides gold in the electrolyte at the end of the operation. Since copper is well soluble in the chloride solution, the accumulation of this metal may be pretty high before solid chloride is precipitated. The purity of the precipitated gold is not diminished by a very large amount of copper in the solution as long as the required absolute quantity of gold is present in the electrolyte. If, however, the same bath is used for continuously treating such alloys, the content of copper must gradually increase to an amount which requires the renewal of the bath. This will become necessary at a relatively early moment if the proportion of copper contained in the anode is high. But I do not think that one is justified to draw therefrom the conclusion which Dr. Tuttle draws—"that any considerable quantity of copper present in the bullion to be treated is undesirable."

The renewal of the solution means, of course, more work, and this means more expense, but the increase is not so great that it should render this operation undesirable. Let the limit of the content of copper in one of the cells, as used in Philadelphia, be 2 kg., then with an average content of 2 per cent of copper in the gold, 100 kg. of this gold-copper alloy could be treated in each cell before the limit of the amount of copper in the electrolyte is reached. This figure is

changed to 50 kg. and 20 kg. if the content of gold in the alloy is 4 or 10 per cent, respectively. Therefore, according to the proportion of copper contained in the material, the cost of the renewal of one solution would have to be charged for treating 100, 50 or 20 kg., respectively, of the raw gold-copper alloy. This cost—exclusive of the value of the copper which could be easily recovered—is certainly not more than \$1.00. Hence, the increase of work due to the accumulation of copper in the electrolyte is no sufficient reason for excluding gold, containing copper, from the electrolytic treatment.

After what I have said it might be advisable to modify to some extent the prognostication of Dr. Tuttle on the prospects of the electrolytic process in the industrial plants of the United States. Dr. Tuttle's remark that gold found in Europe is purer than American gold seems to be correct; for Russian gold, which is by far the largest part of European gold, contains in the average not more than 100 parts of silver. But it seems not correct to base on this fact the assumption that "the success of the electrolytic process will not be the same in the United States as in Europe." In the first line its success has not been very considerable in Europe. The application of the electrolytic gold refining process in Europe is so far limited to the three largest parting plants of Germany, mentioned in my former article. Russian gold would be without doubt perfectly suitable for the direct application of the electrolytic process, on account of its average composition, but it certainly is the very smallest part of all the various materials which the three German parting plants treat. Of these plants, the Norddeutsche Affinerie in Hamburg is—if I am not mistaken—the only one which uses on a larger scale the above-mentioned simple modification of the electrolytic process for the treatment of gold alloys containing a higher proportion of silver.

In Europe, it is not the lack of suitable material which has so far prevented the more extended introduction of the electrolytic methods, but probably the conservatism of the superintendents of plants who do not want to change methods which they have found useful in operation for many years, and who are not well acquainted with the advantages of the electrolytic process. It may be expected that in the United States it is also only necessary to overcome such conservatism in order to pave the path for the introduction of the electrolytic process of refining gold.

Dr. Tuttle doubts that it would be an advantage for the producers of gold in the United States to refine their products themselves by electrolysis, instead of selling it to the mint. He refers to the unavoidable loss of interest which would result from the electrolytic treatment for the producer, and which would be more than the small charge of the United States mint for the treatment. Indeed, in discussing the applicability of the electrolytic method, we would neglect an essential point if we would not take into consideration the question of interest. I will be as brief as possible concerning this point.

The question of interest is of different importance in the following two cases. In the first case, the problem is to use the electrolytic process in place of another one which also yields gold of so high a purity as necessary for practical use. The second and different problem is whether the introduction of the electrolytic process would be of advantage in a plant which has so far sold for cash gold which has not been refined or which has only been incompletely refined. In both cases interest is to be charged for the quantity of gold which must necessarily be contained in the solutions and in the form of rolled gold for cathodes. I find that for any thousand ounces of gold deposited during twenty-four hours by the current, 100 ounces of rolled gold are necessary for the cathodes. Since these are regained after twenty-four hours, the increase of cost per 1000 ounces of precipitated gold is 35 cents.

In about the same proportion gold must be contained in the

electrolyte. In order to calculate how much interest is to be charged for this gold in the solution, if 1000 ounces are to be deposited, we must take into consideration that the solution is generally kept in stock even if the electrolytic operation is interrupted for hours, days or even weeks. The figure which we want to get, is therefore obtained if the yearly interest for the total stock of solution is charged for the total yearly production of gold. The interest for gold in solution, as an item of cost of production, will therefore be smaller or larger, according to the degree in which the available plant is more or less rationally utilized. This is similar as with machines, etc.

Let us suppose that a plant is designed for depositing 3,000 ounces of gold per day, and let 240 ounces be the amount of gold stored in the solution. If this plant is utilized in such a way that the yearly production corresponds to the full work of 300 days, then the yearly interest for the 240 ounces of gold in the solution, charged to the full output of 900,000 ounces of gold, gives the interest of the gold in solution as 33 cents for every 1,000 ounces of deposit. This figure is to be doubled if the yearly output is only one-half. But with such an incomplete utilization of the plant, it would be desirable to precipitate temporarily the gold partly from the solution and to diminish in this way the loss of interest.

The superintendent of a plant, desiring to introduce the electrolytic process in place of another one, has to take into consideration, not only the interest for cathode gold and gold in solution, but also the interest for that part of pure gold which is obtained by electrolysis later than by the chemical process. On the other hand, the producer who is accustomed to sell impure gold for cash, has to take into consideration the total loss of interest caused by the delay in selling the product due to the refining process.

In order to get an exact estimate in this respect, it would not be fair to use the data which Dr. Tuttle has given for the work of the mint in Philadelphia, since it is evident that no special effort is made there to shorten the time during which the material is kept in the electrolytic cells. If my calculation is correct, at least ten days are required for complete consumption of the anodes, according to the practice in Philadelphia. It does not seem to me difficult to devise an industrial modification of the process by which, to a higher degree, the need of the producer is taken into account to reduce as much as possible the loss of interest. With respect to this need, the problem being to treat a given material in as short a time as possible, the thickness of the anode plates must be chosen as small as possible and as high a current density must be applied as possible. With respect to the latter point, the composition of the anode material represents certain limitations. For fine gold 15 amperes and more per square decimeter are well feasible; when the content of silver increases, the current density must be decreased, but even with a content of 10 per cent of silver, the operation is satisfactory with a current density of 9 amperes per square decimeter.

It is also necessary to take into consideration the structure of the material, in choosing the thickness of the anodes to be used at the permissible current density. For fine gold, containing platinum, plates of 4 millimeter thickness are suitable; with coarser gold it is preferable to use a thickness of 5 to 6 millimeters. Under all circumstances, the thickness of the plates and the current density can be so arranged that of the total content of gold in the anodes, 80 to 82 per cent are recovered after twenty-four hours in form of pure gold, in a condition ready for sale or shipment.

The producer who is accustomed to sell his impure gold to parting plants for cash, less the charges for refining, could sell twenty-four hours later 80 per cent of his gold at the full price without any deduction; of the remaining 18 to 20 per cent, 10 to 12 per cent are recovered during the second day and the balance completely on the third, if this portion of the material is used for supplementing the electrolyte, other-

wise in decreasing portions during a few more days. Hence the delay in selling the product due to the electrolytic refining process causes a loss of interest, the main part of which is the one-day interest on the total anode material to which are to be added the one-day interest for 20 per cent of this quantity of gold and a smaller amount for the balance.

The figure for the total loss of interest will, therefore, not be too low, if it is assumed to be  $1\frac{1}{2}$  times the one-day interest of the total gold contained in the material to be refined in the cells. At the present price of gold, and charging 6 per cent interest, this amount would be less than \$5.00 per thousand ounces of pure gold or less than \$4.25 per thousand ounces of raw gold, containing 85 per cent of gold. The idea that this amount would render the electrolytic refining process impracticable for the American producer, would be justified only, if the charges of the American refineries were considerably below the self-cost of parting.

It is scarcely necessary to add that for refineries who subject the product of the sulphuric acid process or of the Moeblus process to a second supplementary refining operation by means of aqua regia, the loss of interest due to the introduction of the electrolytic method of refining the gold would be reduced to one-third the amount given above.

### THE ELECTROCHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

By PROF. H. M. GOODWIN.

During the past year the Institute has equipped a special laboratory for instruction in electrochemistry to meet the demand which the many rapidly growing industries in this branch of applied science have created for men especially trained to undertake the class of problems arising in connection with the development of such industries. As frequent inquiries for a description of the arrangements and equipment of the laboratory have been received during the past winter, it is believed that it may be of some interest and value to those who may be contemplating a similar laboratory equipment to describe briefly the essential features of the arrangements which have been worked out.

The electrochemical laboratory consists of two parts, one devoted to what may be called electrochemical measurements, and to processes requiring currents not greater than about fifteen amperes, and the other to technical work requiring heavy direct or alternating currents up to several thousand amperes. In addition to these two principal rooms, six other special rooms equipped for measurements of electrical conductivity, dielectric constants, physico-chemical quantities, and for research, are provided. These contain no essentially novel features in their equipment, and require, therefore, no special description.

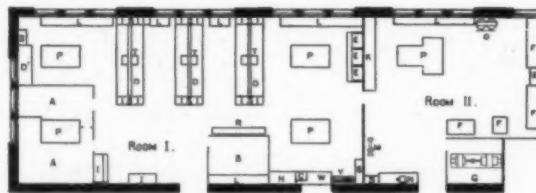


FIG. 1.—LABORATORY OF ELECTROCHEMICAL MEASUREMENTS.

- |   |   |
|---|---|
| A—Private Office.                           | K—Set of ten large Storage Batteries and Switchboard. |
| B—Balance Room.                             | L—18-inch Shelf.                                      |
| C—Hot Closet.                               | M—Grinding and Polishing Machine.                     |
| D—Group of four Students' Desks.            | N—2-hp. Power Motor.                                  |
| D'—Instructor's private Research Desk.      | O—50-kw. Transformer.                                 |
| E—Three Hoods for Electrochemical analysis. | P—Slate-Top Masonry Pier.                             |
| F—Electric Furnaces.                        | R—Reagent Shelves.                                    |
| G—25-kw. Direct-Current Generator.          | S—Sink.   |
| H—Hood.                                     | T—Thermostat.   |
| I—Instrument Case.                          | V—Steam Evaporating Cups.                             |
|   | W—Special Still for Conductivity Water.               |



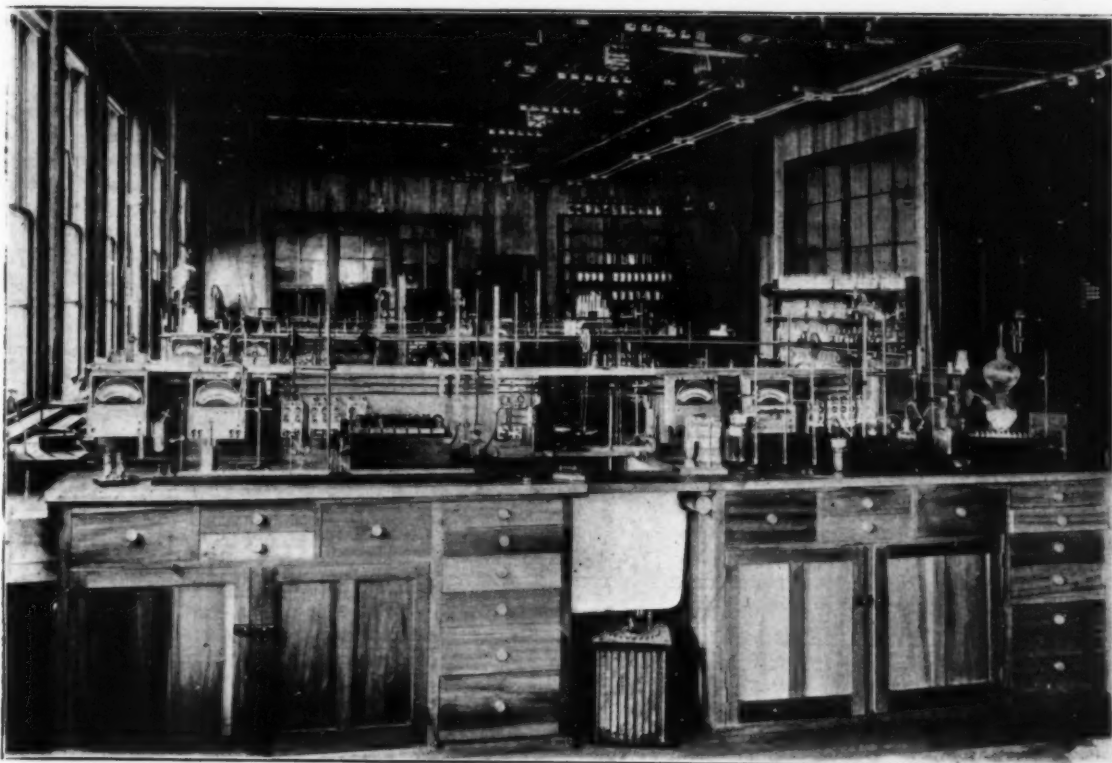


FIG. 2.—GENERAL VIEW OF LABORATORY, LOOKING NORTH, SHOWING ELECTROCHEMICAL EQUIPMENT PROVIDED WITH EACH DESK.

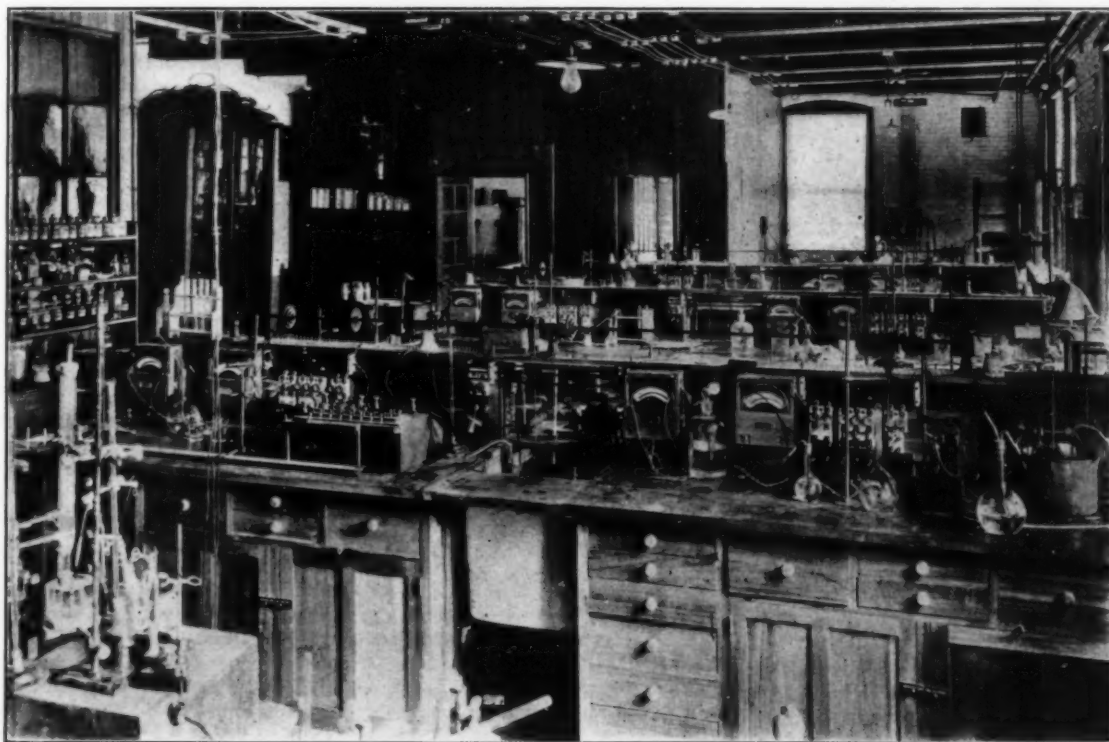


FIG. 3.—GENERAL VIEW OF LABORATORY, LOOKING SOUTH, SHOWING ARRANGEMENT OF DESK CIRCUITS, ETC.

The laboratory of electrochemical measurements (30 x 62 feet), is equipped with desks for twelve students. The general arrangements are indicated in the accompanying plan, Fig. 1, Room I. The most important feature of the equipment in this laboratory is the arrangement of circuits and other conveniences on the desks. These are arranged in three groups of four each with a sink at each end and a large thermostat in the center. Each desk is provided with three faucets, including a Richards suction pump and gas at the sink end. Along the back of each desk is a switchboard, 14 inches high, to which the terminals of the various circuits are brought. Opposite switchboards are separated by a 4-inch space and bridged over the top by a shelf. This permits ample space at the back of each switchboard for the necessary wiring.

The circuits provided are four in number, 110 volts, 12½ volts, 25 volts, and 2 volts, respectively. The first is wired from one side of the general 220-volt direct-current power circuit of the building; the second and third constitute a three-wire system from a special motor generator located at G, Fig. 1; the 2-volt circuit is connected to a large storage cell, four of which, one for each desk, are set up between the desks and

Fig. 4. A constant temperature is then maintained by an ether regulator which operates a relay mounted at the left of the open space above the thermostat. As the temperature of the bath rises or falls above the desired temperature, the relay opens or closes a 110-volt circuit through a 32-c. p. lamp, the bulb of which is nearly completely immersed in the water of the thermostat. The heat thus generated is more than sufficient to compensate for the loss by radiation and evaporation, and has been found to work most satisfactorily. A small 110-volt 1-12 horse-power motor serves to drive in the thermostat a shaft with paddle wheels for stirring the water, and with a device for rotating bottles for saturating solutions. The motor is also belted up to a shaft which runs the whole length of the shelf at the top of the switchboard. The shaft carries four cones of pulleys, one for each desk, by means of which power is furnished to each student for stirring. A heavy brass rod carrying an adjustable arm with a horizontal cone of pulleys equal in size to those on the shaft, can be screwed, when desired, into a brass plate into the top of the desk.

The equipment of electrochemical apparatus provided with each desk is shown in Fig. 2. It consists of a silver, a

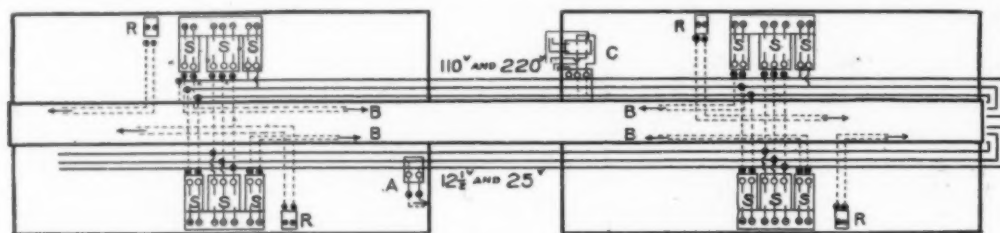


FIG. 4.—DIAGRAM OF WIRING OF DESK CIRCUITS.

A—12½-volt cut-out for charging accumulators for the desks.  
B—2-volt circuit to accumulators.

R—Terminals of rheostat.  
S—General Electric combination switch and cut-out.

C—Cut-out to circuits leading to 1/12-hp motor and to heating coils in thermostat.

under the thermostat. The method of wiring is shown in Fig. 4.

The battery circuits are brought up back of the switchboards as indicated by the dotted lines B. The three-wire 12½ and 25-volt circuit is wired along the top of the switchboard on one side of the desks, and tapped off across to the opposite side as indicated. The three-wire 110-volt and 220-volt circuit is run in a similar manner along the top of the opposite switchboard, and 110 volts tapped off at each desk and across to the proper cut-out on the opposite desk. The circuits are brought out to General Electric porcelain combination switch and cut-outs, connected in turn to large double binding posts mounted on fiber. Each circuit is fused in general for 10 amperes. Currents of this magnitude may be taken from any circuit without affecting adjacent circuits. The fuse plugs in each circuit may be replaced by lamps of different resistances, a set of which permits a convenient and ready adjustment of current within wide limits. For a finer adjustment of current a large rheostat on the floor at the end of each desk, wired to terminals R, on the switchboard, is provided. For a still finer adjustment of resistance, such as is required in tapping off potentials in determining decomposition voltages, a German silver wire or coil with sliding contact is stretched between binding posts along the top of the switchboard. The electrical accessories of the desks are completed by portable Weston ammeters and voltmeters. The general arrangement may be seen in Fig. 3, which gives a general view of the laboratory looking south.

The porcelain lined thermostat, 36 x 18 x 20 inches, in the center of each group of four desks, is heated and regulated electrically. The outside is heavily lagged with magnesia to reduce radiation. To bring the temperature quickly up to any desired value, a heating coil of heavy German silver wire is switched onto the 110-volt circuit at C.

copper, a gas and a titration voltmeter, transference apparatus, complete conductivity apparatus with a resistance box and a slide wire bridge, a Lippmann electrometer, keys, commutators, a potential box and complete accessories for potential work, a three-scale, 3-volt, 15-volt, and 150-volt Weston voltmeter, and a Weston milli-voltmeter, with 15-ampere auxiliary shunt for use as ammeter. The advantage of giving each student a complete outfit at the start is evident; for first, it permits the whole class to work concurrently on the subjects which are being discussed in the lectures; second, it is conducive to great economy of time in the work of the student, and third, it greatly increases the interest and care with which the student undertakes the calibration and standardization of his instruments, if he feels his own responsibility for them throughout all his later work.

The laboratory is provided with a balance room, a hood, a drying closet, steam cups, distilled water, and a large still of special construction for the redistillation of pure water for conductivity work. Three hoods of special construction, each equipped with four different circuits of constant voltage connected with the large accumulators, and with means of regulating and varying their temperature, are provided for electrochemical analysis.

The laboratory for heavy current work, Room II. (30 x 32 feet), is equipped for the purpose of illustrating on a fairly large scale various electrochemical processes involving the use of both direct and alternating currents, and to provide facilities for research work along these lines.

Direct current is supplied from a Holtzer-Cabot motor generator of 25-kw. capacity, shown in Fig. 5. It is enclosed in a room with glass windows to protect it from dust and acid fumes. The motor is supplied with power from the electrical engineering power plant at 220 volts direct current. The double current generator is directly coupled to the motor and

delivers under full load 1000 amperes at  $2\frac{1}{2}$  volts at each commutator, which may be connected either in series or parallel as desired. The voltage may be varied at will by varying the resistance of the separately excited fields. The generator may be switched onto the three-wire system leading directly to

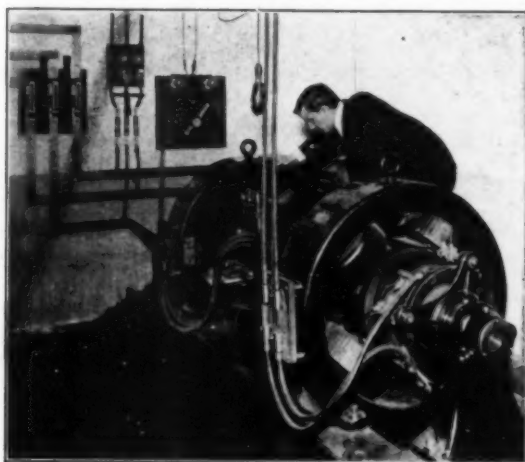


FIG. 5.—25-KILOWATT DOUBLE-CURRENT MOTOR-GENERATOR FOR ELECTROLYTIC WORK.

the switchboard at the front of each desk as already described, or to heavy copper bus-bars 2 inches  $\times$   $\frac{1}{2}$  inch section and 32 feet in length which extend around two sides of the laboratory, 5 feet above the floor. Connection is made between the electric furnaces, which are arranged along the sides of the room and the bus-bars by means of heavy flexible cables which are easily clamped to the latter by heavy screws. The general arrangement is shown in Fig. 6.

For electrolytic work requiring very constant low voltage, and in particular for work which must proceed continuously over night, such as plating, electro-analysis and electro-depositions in general, a set of ten large chloride accumulators capable of furnishing 150 amperes each are provided. These are each connected to a switchboard by means of which any com-

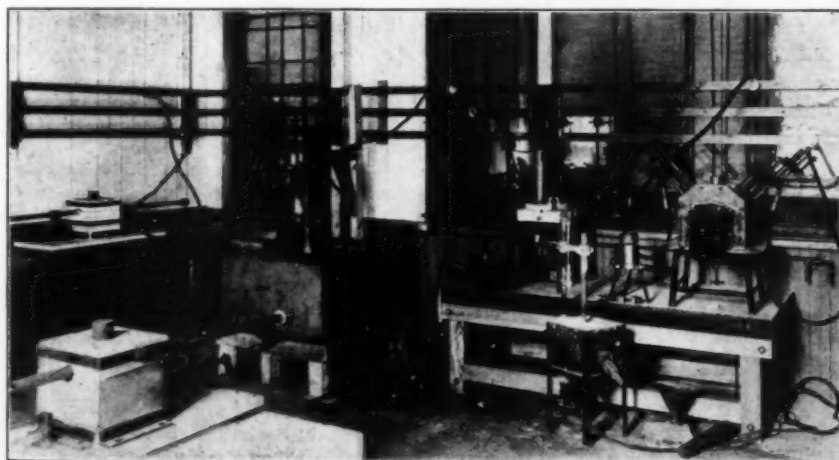


FIG. 6.—ARRANGEMENT OF BUS-BARS AND GROUP OF ELECTRIC FURNACES.

bination of the cells in series and parallel may be easily effected. Currents from 150 amperes at about 20 volts to 1500 amperes at 2 volts are thus available independent of the motor generator. The batteries are charged in series on the 25-volt circuit from the generator.

For furnace work requiring heat only, and for the purpose of bringing to a state of fusion electrolytes to be subsequently subjected to electrolysis, a 50-kw. transformer of special construction is provided. This is of the core type, and can be used on either a 2200 or 1100 volt circuit at 60 or 125 cycles, by connecting the primary windings in series or parallel. At present it is used on a 1100-volt circuit of 125 cycles. There are 16 independent secondaries so wound that each can deliver 300 amperes at 10 volts. The terminals of each of these are brought out to a switchboard where they can be thrown in multiple or series or used in independent combinations as desired. The two halves of the switchboard are quite independent, so that 25 kilowatts can be drawn simultaneously from each set of bus-bars at any voltage from 10 to 80 volts in steps of ten volts. By connecting the two halves in series or parallel, currents from 300 to 4800 amperes at pressure from 160 to 10 volts respectively can be obtained.

Flexible cables, each capable of carrying 500-700 amperes are used to connect the transformer with furnaces which



FIG. 7.—50-KW. TRANSFORMER SWITCHBOARD AND RESISTANCE FURNACE.

cannot be built or brought close to the transformer. Fig. 7 shows the transformer connected for a run on a resistance furnace used in an investigation now being carried out on the properties of refractory oxides. The laboratory is provided with all the necessary accessories to the above power equipment in the way of resistances, choke coils, and direct and alternating current measuring instruments for the measurement of current, voltage and power. The calibration of these instruments and of the student's own desk instruments form a part of the regular work which each student performs in the electrical standardizing laboratory. For measuring high temperatures, the laboratory is well provided with thermo-electric pyrometers. The calibration of these instruments forms a part of the regular work in the laboratory of heat measurements.

The laboratory is equipped with six different types of furnaces, including the Moissan and Borchers types, platinum and graphite resistance furnaces, and a large furnace especially constructed for aluminium reduction. As many furnaces have to be built up for each run, special tables have been designed for this purpose. These contain no



wood in their construction except the supports. The tops are concrete arches supported at the sides by iron I-beams. A layer of fire bricks is placed in sand on the cement, and on this foundation the furnaces are built. No danger from fire has been experienced thus far with tables of this construction.

Finally should be mentioned the typical electro-plating plant with tanks of various size up to 30 gallons capacity for illustrating nickel, copper, silver, gold and brass plating. This includes, of course, the necessary grinding, polishing and finishing accessories.

In concluding the above description of the laboratory which has been equipped to provide special facilities for instruction in electrochemistry, it may not be out of place to indicate the general plan of the course in electrochemistry as given at the Institute. The present four years' course was established by the faculty five years ago, and is given under the direction of the department of physics, that department having inaugurated special instruction in electrochemistry as early as 1894. The chief features of this course are a very thorough training in theoretical and applied electricity and chemistry, together with as much of the subjects of mechanical engineering and metallurgy as can be included in a course of four years' duration.

The work of the first year is common with that of all other engineering courses, and includes mathematics through analytic geometry, mechanical drawing and descriptive geometry, chemistry, language and general culture studies. The latter are continued in all courses, at the Institute throughout the first three years. Specialization begins in the second year in chemistry and electricity. The former consists of qualitative and quantitative analysis throughout the second year and first half of the third year, followed by organic chemistry, gas analysis and assaying in the second term of the third year. These courses all lead up to a very thorough course in industrial chemistry given throughout the fourth year.

Theoretical chemistry is begun in the second year and is continued to the end of the third year. This forms a very thorough preparation for the theoretical and applied electrochemistry, which constitutes a large part of the professional work of the fourth year.

The electrical studies are also arranged in a progressive sequence. Electricity is treated first in the course on general physics of the second year. Theoretical electricity is then begun in the second term of this year, and is continued through the third and fourth years, the later work being devoted to the subject of periodic currents and their applications to alternating current machinery. Parallel with this theoretical work courses are given in electrical measurements and testing, in electrical engineering and in the electrical engineering laboratory.

In addition to subjects included in the two lines of work described above, a certain number of engineering subjects are required. These include metal work, mechanical engineering drawing, mechanism, valve gears and thermodynamics, all leading up to a very practical course in the fourth year on general machinery, including engines, pumps, compressors, etc. Non-ferrous metallurgy, and work in the metallurgical laboratory complete the group of subjects included.

In the last term of the course each student devotes a considerable portion of his time to the preparation of a thesis, embodying the results of an experimental research on some electrochemical subject.

Four years is admittedly too short a time to include in a course all subjects which an electrochemist is likely to find useful in the practice of his profession, and a fifth year, or a graduate course which can be arranged to great advantage, is highly recommended to those who find it practicable to devote another year to study before beginning professional work.

At its recent Commencement exercises the Stevens Institute of Technology conferred the degree of Doctor of Science to Mr. Edward Weston.

## DIMENSIONS OF THE FILMS ON ALUMINIUM ANODES.

By WILLIAM ROY MOTT.

The corrosion of aluminium was shown in a previous paper<sup>1</sup> to be greatly hindered by a film which was better for this purpose, the higher the voltage of its formation. This indicates that the film is thicker the higher the voltage; so definite data upon the dimensions of the film become vital to a careful consideration of film formation at an aluminium anode, especially since the film constitutes the essential part of the aluminium electrolytic rectifier and condenser. The thickness of the dielectric determines the capacity of the condenser. Since the thickness of the film varies greatly according to voltage and electrolyte, it is not surprising that the measurements of the capacity made by Franchetti, Nodon, Mitkiewicz and Zimmerman are widely at variance. Campbell and Gahl have also found that they did not get concordant results. Hence, the thickness of the film is of practical importance, as well as theoretical.

The thickness of the film is the object of investigation considered in this paper. The weight of the film and coulombs required for its formation is the first phase of the subject.

### ANODE GAINS IN WEIGHT.

When weighed sheets of aluminium are used as anode in a saturated sodium acid phosphate solution it is well known that the aluminium tends to insulate itself. Even with a pressure of one hundred or more volts, very little current flows. That this is due to the aluminium and not to the resistance of the electrolyte may be proved by measuring the resistance of the electrolyte with lead plates and getting the CR line, and it is found that the CR drop is less than 1 per cent of the total drop. In forming these plates, considerable current flows at the start, but in a few minutes decreases very greatly. In four experiments (the results are given in Table I. and II., the aluminium plates were weighed to a tenth of a milligram before and after and were found each time to gain in weight. At anodes the tendency of metals is to go into solution, hence the gain in weight of the anode does not come from a metal plating out of the solution. The question arose as to whether, at the contact of the solution with the air and the aluminium, there was any marked gain or loss. To find this out, the area of the exposed part was decreased by thirty times; the proportionate gain in weight was not appreciably affected. Plate II. was treated as anode and cathode several times, and then finally used as anode and found to have practically the same weight as when weighed as anode the first time. Plate III. was run as cathode for awhile (two minutes, 2.5 amperes). It was found to have lost two milligrams, which left two and two-tenths milligrams gain over the original weight.

The aluminium Plate II. was now run as anode and about twenty coulombs were required to re-form it. This is one-sixth the number of coulombs required for the original formation. (The starting current was about 5 amperes, which fell in ten seconds to 0.1 ampere). Now, leaving the plate an open circuit for ten minutes, it was observed on closing the circuit that about two coulombs were required for reformation. As nearly as I could estimate it, the starting current was 0.9 amperes, which fell to the normal leakage current in from one to two seconds. The weight was now found to be 7.8905 gs. or 0.1 milligram greater than at the last weighing, when it was the cathode. Aluminium Plate III. was, after having been formed as anode and properly washed and dried and weighed, left out of the solution for about an hour to find out how many coulombs would be required to reform it. On testing, the initial current was found to be small, and this decreased in a few seconds to the normal leakage current.

These experiments upon the four aluminium plates show that there is a real gain in weight of the anode due to the

<sup>1</sup> The Corrosion of Aluminium and its Prevention. ELECTROCHEMICAL INDUSTRY, April, 1904.

formation of the film which is fairly permanent. The disappearance of the resistance offered by an aluminium anode cannot be used as evidence (as Lecher and some others have done) that the film has been dissolved.

A fair criticism of these experiments would be that the actual weighings are greatly in error because of adhering moisture. In the case of weighing glass beakers, errors of consid-

Further experiments were made to determine the effect of the voltage upon the thickness of the film which was formed as rapidly as possible by the proper manipulation of the resistances in the circuit. The plates after being formed were dried and weighed. The weighings<sup>1</sup> were done by the method of swings. In the following experiment, the same plate was first formed at 20 volts, then at 40 volts and finally at 60 volts.

TABLE I.

GAIN IN WEIGHT OF ALUMINIUM ANODE.*				
Number of Plate.	I.	II.	III.	IV.
Thickness <sup>1</sup> .....	.0086	.0150	.0150	.0150
Area of plate <sup>2</sup> ..	145.	135.	140.	190.
Width <sup>1</sup> .....	14.5	13.5	14.	0.35
Weight before <sup>3</sup> ..	4.7567	7.8865	8.7561	7.0995
Weight after <sup>3</sup> ..	4.7607	7.8924	8.7622	7.1085
Gain <sup>3</sup> .....	.0040	.0059	.0061	.0090
Gain per sq. dm. <sup>3</sup>	.0027	.0044	.0044	.0047
Gas at cathode <sup>4</sup>	12.	12.	10.	12.5
Coulombs <sup>5</sup> .....	130.	135.	120.	115.

<sup>1</sup> Centimeters. <sup>2</sup> Square centimeters. <sup>3</sup> Grams.

<sup>4</sup> Gas given off at cathode is measured in cubic centimeters. One cubic centimeter, by experiment at this temperature, corresponds to a passage of about ten coulombs.

<sup>5</sup> These coulombs were obtained by integrating the current-time curves for the formation of the film. (See Table II.).

\* The plates were formed at 125 volts, direct current, in a saturated solution of disodium hydrogen phosphate and at room temperature.

TABLE II.

## MODE OF FORMATION OF FILM.

Plate I.			Plate II.		
Time, Seconds.	Amperes.	Volts.	Time, Seconds.	Amperes.	Volts.
0	7.	50	0	7.	...
10	3.	70	10	2.	88
20	1.5	95	20	1.5	...
30	.9	...	30	.9	92
40	.5	...	40	.6	117
50	.3	...	50	.4	121
60	.3	...	60	.3	...
120	.1	125	120	.2	125

Plate III.			Plate IV.		
Time, Seconds.	Amperes.	Volts.	Time, Seconds.	Amperes.	Volts.
0	7.	33	0	5.	30
10	2.4	96	10	2.5	72
20	1.2	112	20	1.5	80
30	.6	120	30	.9	89
40	.4	124	40	.7	91
50	.2	124	50	.6	103
60	.1—1/2	124+	60	.3	114
120	.1	125	120	.2	125

erable magnitude may be made, due to this cause. For this reason, the author ran blank experiments, both upon the unformed and the formed aluminium plates. No variations greater than one-tenth milligram were observed. But the most conclusive proof of the permanence of the film in air was found in drying 39 milligrams of the detached film. The greatest extremes of drying conditions had an effect of less than 3 per cent.

The formation of the film is accompanied by more or less corrosion of the anode. This is an important factor. It seems to have been overlooked by Cook in some experiments on aluminium electrodes in sulphuric acid. His experiments do not justify his position that the film is an oxide. This point will be more fully considered later. This corrosion of the anode is usually small during the formation of the film, but nearly all the leakage current (the steady current) that flows after the film is formed is corroding. So all the results by this method give *minimum* values of the calculated thickness of the film.

TABLE III.

## ALUMINIUM PLATE FORMED IN SATURATED DISODIUM HYDROGEN PHOSPHATE.

Original weight (grams) .....	3.94212
Formed at 20 volts .....	3.94516
" at 40 volts .....	3.95023
" at 60 volts .....	3.95041
Increment in weight at 20 volts .....	+ .00304
" at 40 volts .....	+ .00507
" at 60 volts .....	+ .00018
Total gain in weight at 20 volts .....	.00304
" at 40 volts .....	.00811
" at 60 volts .....	.00829

Each time the plate was washed (in distilled water), dried and weighed. The results are given in the following table III. and are plotted on Fig. 1.

This series of experiments were made on plates of 100 sq. cm. area (an area of surface of 200 sq. cm.). The rate of

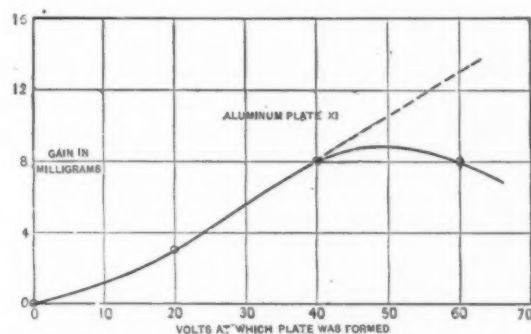


FIG. 1.—INFLUENCE OF VOLTAGE OF FORMATION UPON THE FILM.

corrosion at 60 volts appears to balance the rate of gain of the anode. This was duplicated with other similar experiments which it is not necessary to give here.

Calculation of gain in thickness of the aluminium plate, and calculation of the thickness of the film can now be made. Ordinary hammered aluminium has a specific gravity of 2.67. Bauxite has a specific gravity of 2.55. The aluminium hydrates have a specific gravity greater than 1.0. Assuming that one cubic centimeter of this film weighs two grams, then one milligram will occupy .0005 cubic centimeters; where we have both sides of a plate with an area of 100 sq. cm. on a side, the thickness of the film would be .0000025 cm. Factors of variation are, specific gravity of the film (between 1.0 and 2.5); the proportion of aluminium in the film which, of course, added nothing to the weight of the plates; and the actual loss of material by corrosion. The gain in thickness of the aluminium plate is not the sum of the thickness of the films on both sides, but only a fraction of this, inasmuch as some of the aluminium goes into the formation of the film.

If we assume that the film contains 40 per cent aluminium<sup>2</sup>, then we must add 80 per cent to the observed gain in weight.

Calculated out on these assumptions, the thickness of the

<sup>1</sup> These weighings were made by Dr. Patten, for which I thank him for his kindness in doing this.

<sup>2</sup> A reasonable value, in view of the various chemical analyses that have been made of the film.

film formed on an aluminium anode in phosphate solutions is as follows:

Voltage.	Thickness.
20 volts.	.000014 centimeter.
40 "	.000037 "
60 "	.000038 "

At 60 volts, the film is really thicker than at 40 volts. In fact we may assume a rate of increase in weight of about 4 milligrams (for 100 sq. cm. of aluminium plate) for every rise of 20 volts, so at 100 volts we would expect a thickness of about .00010 cm. This would be in accord with the other data. The next consideration is the coulombs required for the formation of the film.

#### COULOMBS TO FORM THE FILM.

The film forms to a certain thickness for each particular voltage, but at the same time Faraday's law must be obeyed. At higher voltages the film becomes thicker and more current is required to cause this increase in thickness. Table II. and the following table IV. give data upon the current-time curve for different voltages.

TABLE IV.  
FORMATION OF THE FILM.<sup>1</sup>

Time.	5 Volts.	10 Volts.	20 Volts.	50 Volts.	Volts.
Sec.	1 2	3 4	5 6	7 8	9
0	.070 .070	.150 .150	.200 .200	200 ...	240
10	.010 .010	.020 .020	.055 .040	100 130	...
20	.004 .004	.010 .010	.020 .020	60 ...	...
30	.003 .003	.004 .004	.012 .010	38 30	60
40	.002 .002	.003 .003	.007 .007	20 20	...
50	... ..	.002 .002	.004 .003	17 ...	...
60	... ..	... ..	.003 .002	12 ...	4

<sup>1</sup> Readings were taken with aluminium strips with an area of ten square centimeters. In specimens 7, 8, and 9 the current was adjusted by resistances so as not to exceed the limit of the millimeter. The results are given in amperes. All these strips were formed with direct current.

Integrating the preceding table, IV., for the coulombs, the following results are obtained and tabulated below:

Number of Specimen.	Formed at: Volts.	Coulombs.
1	5	.8
2	5	.8
3	10	1.9
4	10	1.9
5	20	3.0
6	20	3.8
7	50	2.8
8	50	4.5
9	100	...
n	120	10.0

From these coulombs, we may calculate the thickness of the film if we know its composition. The film is not an oxide, but in the case under consideration the film varies between the limits  $\text{Al}(\text{OH})_3$  and  $\text{AlPO}_4$ . The chemical composition of the film will be discussed more fully in a future paper.

The thickness of the film that forms on aluminium anodes in phosphate solutions has been calculated from the coulombs. The results are given below:

Voltage.	$\text{Al}(\text{OH})_3$ Centimeters.	$\text{AlPO}_4$ Centimeters.
10	.000013	.000025
50	.000032	.000063
120	.000064	.000126

Calculated thicknesses are given in the above table for the limits of chemical composition.

The other methods of obtaining the thickness of the film are

by mechanical measurements of the film, by optical methods from interference colors and by detaching the film.

The author has tried a variety of methods of measuring the thickness of the plate mechanically by means of a self-setting micrometer-screw caliper. This instrument read to .0001 cm. Several experiments seemed to indicate that the aluminium plate was just a little thicker where the film was formed than where there was no film. These readings are too close to the limits of error to be of any value by themselves. Results obtained with a spherometer were not satisfactory, because of the flexibility of the aluminium plates. By repeating this experiment with firm plates more satisfactory results would probably be obtained.

#### COLORS OF THIN FILMS.

Films formed on aluminium anodes show interference colors which have been used by Mr. C. I. Zimmerman for calculating their thickness. But before taking up the special case of aluminium anodes, it may be well to consider how general is this film formation. In 1826, Nobili observed that lead acetate gave chromatic rings (called Nobili rings) upon anodes, due to the precipitation of thin films of lead peroxide. Others (among whom Becquerel and Gassiot may be mentioned) introduced interesting and valuable variations into Nobili's process. Copper oxide (Buchner, Watt and others) may be precipitated in the same way. Böttger and Ludersdorff have succeeded in producing upon zinc, films that show interference colors. Oxides of manganese, bismuth, cobalt, nickel, etc., have been formed by Watt into thin films that show rich interference colors. A complete list of the workers in this field would be very long<sup>2</sup> indeed. In recent years the French papers have given much attention to this branch of electrochemistry. (See *L'Electrochimie* and *Chronique Industrielle*.) These references show that films of metallic oxides formed by electrochemical means are common. The films that form on aluminium anodes have some similarities to this class of films; but they are unique because of their enormous dielectric strength.

These films, formed on aluminium anodes, show interference colors, as has been pointed out by Beetz, Pollak, Norden, Isenberg and others. Mr. C. I. Zimmerman has been the first to apply optical methods to the measuring of the thickness of these films. He says: "By means of these interference color phenomena, the writer has estimated the thickness of the films. They range from less than 0.000005 cm. to, in exceptional cases, more than 0.000050 cm. in thickness."

Mr. Zimmerman has given the color changes for increasing thicknesses of the film, but he has omitted the changes in color obtained on rotating the plate. In the well-known equation<sup>3</sup>

$$n\lambda = 2T \cos B$$

there are two variations that may produce the same result. The colors observed for a given thickness,  $T$ , on varying the angle  $B$  can pass through only a limited number of changes. The one exception to this statement occurs when the index of refraction approaches unity, but this case need not be considered for the most probable value of  $i$  appears to be 1.5 for these anode films. The corrections to be made if  $i$  is not 1.5 are as follows. If  $i$  equals 2.0, add 20 per cent; but if  $i$  equals 1.3, subtract 30 per cent. The solution of problems by the above equation is best done by first solving many trial cases. The limiting value of  $\cos B$  should be calculated. A complete presentation of these optical methods would be long, tedious and out of place, so we will give the experimental data and the conclusions.

<sup>2</sup> See Elsas, *Wied. Ann.*, 29, 331, 1886. A. H. Hiorns, *Text-Book on Metal-Coloring and Bronzing*, 1892. M. Paul Malherbe, *Metal-Coloring and Bronzing*, M. Paul Malherbe, Translation from the French, in *Scientific American Supplement*, No. 1473, March 26, 1904. Rieder, *Zeitschrift für Elektrochemie*, 9, 911, Nov. 18, 1903.

<sup>3</sup> In this equation, the terms signify quantities as follows:

$n$  = integral number of wave lengths in air.

$\lambda$  = wave length of light in air.

$B$  = angle of incidence on the second surface of the thin plate.

$T$  = thickness of thin plate.

$i$  = index of refraction.



In table VI. the author gives his observations upon films formed in disodium hydrogen phosphate. Column I. contains the colors observed holding the aluminium plate at right angles to the line of sight; and column V. contains the colors

TABLE VI.

COLORS OF ALUMINIUM PLATE FORMED IN SATURATED DISODIUM HYDROGEN PHOSPHATE ( $\text{Na}_2\text{HPO}_4$ ).

Volts.	Colors on rotating.				
	I.	II.	III.	IV.	V.
0	white	white	white	white	white
25	blue	blue	blue	blue	red
50	yellow	green	yellow	green	green
75	brown	brown	green	green	red
100	blue	purple	purple	blue	green

observed when the plate had been rotated so as to appear nearly on edge. Columns II., III. and IV. give the colors seen for intermediate degrees of rotation.

The two methods of calculation yield concordant results. At 25 volts, the calculated value of the thickness of the film formed in phosphate solution is .00002 centimeter, and at 100 volts the calculated value is .00008 centimeters.

## DETACHED FILMS.

It was necessary to find a way of removing the metallic aluminium and yet of leaving the film intact. For this purpose, aluminium anodes that had been formed at 125 volts in disodium hydrogen phosphate were used as anodes in a copper sulphate solution. Current was passed until holes from 1 to 3 millimeters diameter had been eaten through the aluminium sheet. The smaller holes, on rinsing the sheet in distilled water and drying, had transparent, colorless films still intact. I detached some of these, put them in a test-tube where they floated around like plates of mica and showed iridescence similar to that displayed by the original aluminium surface, when

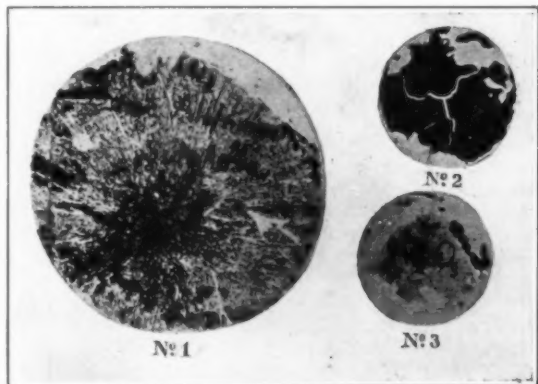


FIG. 2.—PHOTOGRAPHS.

No. 1.—Basic aluminium film formed by using aluminium foil as anode in dilute sulphuric acid. (This photograph was taken by Mr. Bellinger, whom I wish to thank.)—No. 2.—Original aluminium foil.—No. 3.—Aluminium oxide (suboxide) formed by aluminium foil in gas flame. This contains a film of transparent aluminium, since it can be burnt, it conducts electricity, and in reflected light gives the lustre and appearance of metallic aluminium.

viewed from different angles. On the large holes, a rim of film was generally left on each side. Cutting some of these holes through their center and examining under a microscope, the edge of the film was visible. In a film which I could sharply focus, the thickness did not appear much greater than the cross-hairs in the microscope, hence, from this I should judge the thickness to be .0005 cm. or less.

Professor C. E. Mendenhall kindly undertook to measure the thickness of the film. This was done by placing three of the films that bridge the holes in the aluminium plate between two

plates of glass. The thickness was found by a direct-vision spectroscopy to be 0.0007 centimeter or less. This was for a film formed on an aluminium plate at 125 volts in a saturated solution of disodium hydrogen phosphate, at room temperature.

The thickness obtained by these two methods were much higher than expected. The reasons for this result are, first, the film tends to crumple and fold somewhat, and, second, it is probable that the film became *thicker* in the copper sulphate under the action of the current. Another method of obtaining the film separate from the aluminium is to form the film on a very thin sheet of aluminium.

At the Washington meeting of the American Electrochemical Society, the author showed some transparent films that had been formed out of an anode of aluminium foil. This aluminium foil had a thickness of .00008 centimeter. The author has formed transparent films, both with sulphuric acid and phosphoric acid. This shows that films of the thickness .00016 centimeters may be formed. Further results of value may be expected by a systematic use of this method.

The electrolyte causes large variations in the thickness of the films formed on aluminium anodes. Sulphates give thickest films and citric acid thinnest films. These considerations hold only where comparison is made at the same voltage. From Cook's experiments upon gain in weight of aluminium anodes in sulphuric acid, the author has calculated the thickness of the films and finds them several times thicker than the films formed in phosphate solutions. Again, optical methods show that a film formed at 20 volts in sulphuric acid is *thicker* than a film formed at 100 volts in a phosphate solution.

## SUMMARY.

In this investigation it was necessary to use as many methods as possible for measuring the thickness of the film that forms on aluminium anodes. The gain in weight of the aluminium anode gives the minimum limits of the thickness, while the coulombs required for the formation of the film gives the maximum limits. The thickness can also be calculated from the interference colors. This method is the easiest and most accurate means of comparing films formed in different electrolytes, at different temperatures, etc. The most valuable method for obtaining the absolute thickness is the actual separation of the film from the aluminium. A suitable solvent for the aluminium is required. The use of formed aluminium plates in mercury may solve the problem. Aside from chemical means there is the electrical one of using the aluminium as anode and cathode alternately, so that the film is loosened. Another device is the use of aluminium foil as anode.

In conclusion, the film that forms on aluminium anodes may be said to be roughly a linear function of the voltage. On this basis the thickness of the film in phosphate solution is as follows:

Volts.	Thickness. Centimeter.
1	.000001
20	.00002
80	.00008
320	.0003

The usefulness of this work is apparent as regards the aluminium electrolytic condenser; but in other directions it is also important. Many formulas have been deduced by various experimenters to express the polarisation of aluminium anodes, but these are only *empirical*, since they have no foundation in the properties and dimensions of the insulating film. A further study of this film may reveal the real mechanical and electrical forces that act on molecules and ions at the moment of electrolytic separation. Anodes of other metals need study; this is particularly true of chromium, which has been assigned such a unique position by Hittorf and by Morgan and Duff.<sup>1</sup>

<sup>1</sup> Jour. Am. Chem. Soc., 22, 33 (1900).

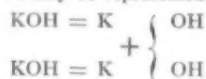
# A CONTRIBUTION TO THE THEORY OF THE JUNGNER-EDISON ACCUMULATOR WITH CONSTANT ELECTROLYTE.

By M. U. SCHOOP.

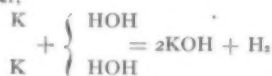
## I.

In *Electrical World and Engineer* of June 29, 1901, Dr. E. F. Roeber has developed a theory showing that if an alkaline accumulator with constant electrolyte (so-called "oxygen-lift cell") is charged or discharged, considerable concentration changes must occur at the electrodes, due to the different migration velocities of the K and OH ions. However, the total content of KOH in the electrolyte—or in other words, the average concentration of the electrolyte—remains constant during every phase of charge and discharge. Therefore, when the concentration of the solution in the pores of one electrode increases, the concentration in the pores of the other electrode must simultaneously decrease. Of course, as soon as gas is developed at the end of a charge, water is decomposed and the concentration of the electrolyte is thereby changed.

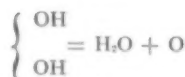
If two molecules KOH are decomposed by the current, the reaction may be represented by the following formulas:



further,

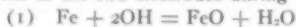


and

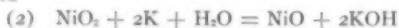


H<sub>2</sub> and O reacting with the active materials at the two electrodes.

If, for instance,  $2 \times 96,540$  coulombs pass through the battery ( $96,540$  coulombs = electric charge of one monovalent gramion), two monovalent gramions OH are involved in the reaction at the negative (iron) electrode, and two monovalent gramions K in the reaction at the positive (nickel) electrode. We may write, according to Roeber's suggestion<sup>1</sup>, the reactions at the two electrodes during discharge of the battery



and



These equations, in combination with the above equation of the reaction, show at once that after  $2 \times 96,540$  coulombs have passed, one molecule of water has been formed at the iron electrode and simultaneously one molecule of water has disappeared at the nickel electrode so that the electrolyte has become more dilute at the iron electrode and more concentrated at the nickel electrode. The result of the electrolytic action would, therefore, be a simple electrolytic transfer of oxygen from the nickel electrode (where the oxygen must be assumed to exist under high pressure) to the iron electrode (where the oxygen must be assumed to exist under low pressure).

On the basis of the value 0.25 for Hittorf's transport number of K in a 30 per cent KOH solution, Roeber arrives at the following final result. When the battery gives out in discharge one coulomb, the changes in the battery due to the migration of the ions and to the electrochemical processes at

the electrodes, consist in the transfer of  $\frac{1}{2 \times 96,540} = 0.000052$

grammolecule O or 0.000083 gram O from the nickel plate to the iron plate, the transfer of 0.000026 grammolecule KOH = 0.000146 gram KOH from the solution at the iron

<sup>1</sup> In reality both active materials at the end of a charge of the battery are surely hydrates; anhydrides are electrolytically inactive. Jungner writes for the charged active iron material  $\text{Fe} + (\text{HOH})_x$  and for the charged active nickel material  $\text{NiO}_2 + (\text{HOH})_y$ .

terminal to the solution at the nickel terminal, and finally the transfer of 0.000052 grammolecule H<sub>2</sub>O or 0.000094 gram water from the solution at the nickel terminal to the solution at the iron terminal. This result is entirely independent of the chemical nature of the metals used for the electrodes, as long as we have to do with this type of battery, with a constant total concentration of KOH solution.

## II.

The correctness of Roeber's theory can be proven by experiments. It is the purpose of this article to call attention to an experimental method, not yet well known, which was suggested by Dr. E. Sieg and worked out by the author, and to discuss some results of a great many measurements made with this method with nickel, iron and cadmium electrodes.

The method consists essentially in the measurement of the changes of weight, caused by electrolysis in the electrodes (including the electrolyte in their pores). This may be done either by weighing an electrode on a scale before and after the passage of the current, or by suspending the electrode to be tested between two corresponding opposite electrodes from the beam of a suitable balance, as shown in Fig. 1. The latter method was used in these experiments.

Let us designate with H the volume of the pores in the

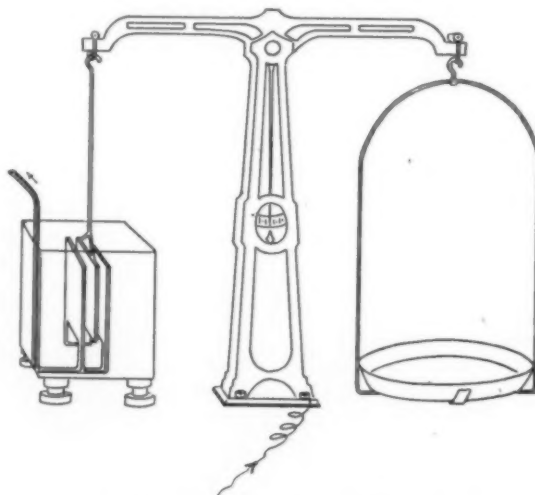


FIG. 1.—BALANCE FOR STUDYING CONCENTRATION CHANGES AND DIFFUSION PHENOMENA IN STORAGE-BATTERY PLATES.

active material of an electrode. These pores are filled with electrolyte. At the moment in which we begin the discharge, the volume H of the pores may be = H<sub>0</sub>. We then get for any moment

$$H = H_0 - vit$$

where *t* is the time in hours after the current has begun to pass, *i* the constant discharge current in amperes, and *v* the increase of volume of the active mass per ampere-hour. Since the volume of the pores filled with liquid changes, the weight of the liquid in the pores also changes, and the decrease of weight, due to the decrease of volume of electrolyte, is *vits*<sub>0</sub>, where *s*<sub>0</sub> is the specific gravity of the solution at the beginning of discharge.

Another change of the weight of the liquid which fills the pores of the volume H, is due to the fact that the concentration of the liquid is different at the beginning and at the end of the experiment. This increase of weight during the time *t* is  $-(s_0 - s)(H_0 - vit)$

where  $-(s_0 - s)$  represents the increase of specific gravity of the liquid in the pores during the experiment.

We may assume that the change of absolute weight of the

solid electrode is 0.3 grams per ampere hour (solely due to the lifting of oxygen from one plate to the other); this will probably be very nearly correct.

By the addition of the different items which make up the total change of weight, we now get the total change of the absolute weight  $p$  in grams.

$$p - p_0 = \pm (0.3 - v s_0) i t \mp (s_0 - s) (H_0 - v i t)$$

where  $p_0$  is the weight of the electrode at the time  $t = 0$ .

This formula gives the absolute change of weight of the electrode, inclusive the weight of the liquid in the pores. This change of weight of an electrode during discharge might be determined by removing the electrode from the liquid, allowing the liquid to drop off for a certain time and then placing the plate on a scale. But it would be impossible to analyze the different items making up the total change of weight by this method. Moreover, this method is not accurate. Much more accurate results, which agree among themselves much better, are obtained by the other method already noticed, in which the change of weight of the electrode is measured in the electrolyte itself.

With this method it is, of course, in general, necessary to take into account the loss of weight of the electrode equal to the weight of the displaced electrolyte. For our present case, however, in which the electrolyte between the two plates (outside of the pores) has a constant concentration for the whole time of a discharge or charge, the above formula is exact without further terms of correction. On the other hand, in experiments with lead electrodes in  $H_2SO_4$ , this point must be duly taken into consideration, since the loss of weight of the electrode in the acid solution equal to that of the displaced acid, will be quite different at the beginning and at the end of the discharge on account of the fact that the concentration of the external acid solution has changed.

The question as to the formulas which we have to give to the active materials during the reaction of the alkaline accumulator has not yet been definitely settled, nor do we know exactly the specific weights of the nickel and iron hydrates. It is therefore not yet possible to give exact numerical data for the various items in the above equations. The value of the following experiments is to be found mainly in the experimental proof of the concentration changes of the solution in the pores of the electrodes, taking place during and after the passage of a current.

The method using a suspended electrode<sup>3</sup> offers the advantage that it is not necessary to take the electrode out of the electrolyte in order to determine the variations of its weight, nor is it necessary to open the circuit. The balance used in this method should be rather compact, but should, nevertheless, have sufficient sensibility. The bearings are preferably made of hardened steel and it is then possible to introduce the current to the suspended electrode from the external circuit, through the stationary frame of the balance; this is a requirement of great importance for the successful application of the method. A large e. m. f., in form of a storage battery of about 300 ampere-hours capacity was connected in series with the cell, so that it was easy to modify the requirements of the experiment at will; this is not possible, if, as usual, the cell is discharged through a wire resistance; moreover, there is not the inconvenience of being obliged to regulate the resistance continually in order to keep the current constant.

The following quantities were measured:

(a) The voltage at the terminals of the whole accumulator.

(b) The voltage of the suspended electrode against a small auxiliary nickel or iron plate.

(c) The change of weight of the suspended electrode during the passage of the current and after interruption of the current.

<sup>3</sup>See also Ein Beitrag zur Kenntnis der Diffusionsvorgänge an Akkumulatorelektroden. By M. U. Schoop. Stuttgart; F. Enke, 1903.

(d) The temperature of the electrolyte.

(e) The current.

In order to avoid any variations of temperature during the passage of the current, a large glass vessel was used as container. This also offered the advantage that it was possible to see any gas bubbles on the plates, any changes in color of the electrodes or the electrolyte, and to observe any particles of active mass dropping off or carried out of the pockets.

Moreover, it is not only possible to measure the changes of weight and volume of each electrode, but also to study conveniently the phenomena of diffusion—which are so important for many electrochemical purposes—during and after electrolysis. Attention may here be called to the comparative experiments<sup>2</sup> made by the author with a positive Plante plate and a positive pasted plate, both plates having exactly the same capacity for a one-hour discharge; these experiments prove the great difference in the speed of diffusion between the acid in the pores of the plates and the outside solution.

It is true that in the alkaline accumulator the diffusion of the electrolyte is probably not of such fundamental importance as is the case with the lead accumulator, since in the latter case the chemical reaction which furnishes the electrical energy is the change of the active masses into lead sulphate. Nevertheless, such tests of nickel or iron electrodes are very valuable, since it thus becomes possible to directly observe in a most simple manner not only the concentration changes of the liquid in the pores, but also the volume changes of the active masses, as is evident from the above formulas.

While the good diffusion of the acid in the lead accumulator has been stated to be the vital condition for the perfect operation of the lead cell, we may say correspondingly that the maintenance of good contact between the active mass and the support plates through which the current passes to the active mass from the external circuit, is the vital requirement for the good behavior of the alkaline accumulator. This will be evident, if we take into consideration the well-known very low conductivity of the active materials which, to get a better conductivity, must be mixed with graphite and subjected to strong pressure. It is thus clear why it must be of the greatest importance to ascertain the variation of the volume of the active materials, since the phenomenon of the expansion and contraction of the active materials must be intimately connected with the change of the total conductivity of the active materials.

There is no doubt that the exact knowledge of the variations of the volume of the active masses is also of importance for the lead accumulator, although disregard of this point leads to other consequences, since it will result in a dropping off of active material and in a distortion of the plates. It is peculiar that in the literature on the lead accumulator the variations of the volume of the active materials has nearly always been neglected; as an exception I mention the well-known book of Dolezalek on the theory of the lead accumulator.

The final result of the electrolytic action of the lead accumulator during discharge consists in the formation of lead sulphate on both electrodes and simultaneously there is rather a considerable increase of volume on both plates. We will find that the opposite is the case with the electrodes of the alkaline accumulator; in this case there is a diminution of the volume of both electrodes during discharge and an increase of volume during charge; this change of volume is small with the iron and cadmium electrode, but considerable with the nickel electrode, and in this case it is the greater, the more the plate has been discharged.

### III.

The electrodes used in the experiments were taken from an old Jungner accumulator. All had the same dimensions, namely, 75 x 200 x 5 mm. The electrodes consisted each of

<sup>2</sup>Elek. Zeit., Heft 12, 1903.



three pocket units, made of perforated nickel-steel and containing in their interior the active materials. The three pockets were placed side by side and clipped at the top and bottom by means of folded strips of the same material. (The electrodes now made by the Jungner-Akkumulator Aktiebolaget in Sweden are somewhat different, and have proven better, especially concerning the voltage drop).

The first experiments were made with a cell which consisted of two nickel electrodes and an iron electrode, the latter being suspended on the scale. As auxiliary measuring electrode a fully charged small plate of nickel was used which after completion of the charge, showed an e. m. f. of 1.5 volts against the iron electrode, after four days, however, only 1.35 volts; after this time this value remained constant and the auxiliary small plate remained continually in the cell.

The color of a charged iron electrode is distinctly dark brown. During discharge the color changes to a dark olive green. The charged nickel electrode shows generally a light brown shade, which, however, does not interfere with the bright lustre of the outer surface and which soon disappears, after the discharge has begun. The brown oxide film of the auxiliary nickel electrode did not disappear even after it had been used for several months.

#### DISCHARGE OF THE IRON ELECTRODE WITH 0.5 AMPERE

Of many measurements made with iron electrodes, I will first give the following results, represented by the curves in

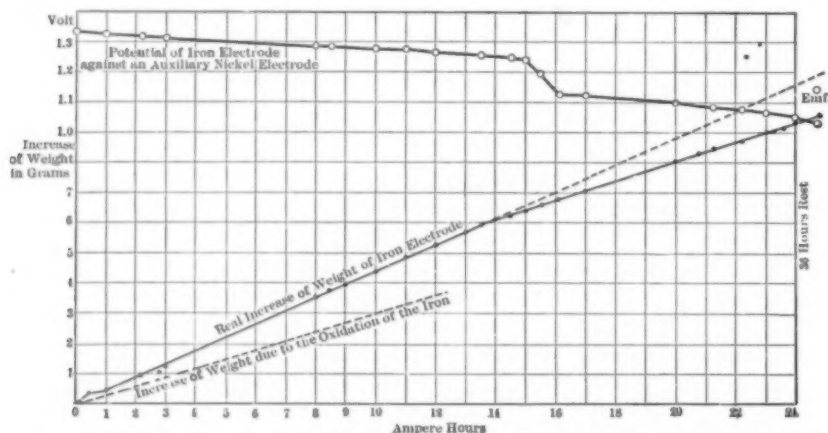


FIG. 2.—BEHAVIOR OF IRON ELECTRODE WITH LOW DISCHARGE RATE (0.5 AMP.)

Fig. 2. This was an extraordinarily slow discharge of about fifty hours ( $i = 0.5$  ampere) and care had to be taken to keep the temperature of the room constant; regulation of the current did not become necessary as a result of the arrangement of the experiment with the battery mentioned above.

The discharge voltage of the iron electrode started with 1.34 volt; within thirty hours (corresponding to 15 ampere-hours) the voltage decreased gradually and slowly to 1.2 volts; it then dropped rapidly and assumed a value of about 1 volt, which it maintained for a long time. After 24.7 ampere hours were given out by the cell the value 1.03 volt was reached. Since the main purpose of the experiment was to determine the changes of weight of an iron electrode if discharged with a very small current, the experiment was now discontinued.

The phenomenon of a "double voltage" (indicated by the sudden bend near the center of the discharge curve) is observed not only with the iron electrode, but also with nickel electrodes. With the latter, however, I have observed the sudden bend in the voltage curve only at the end of the discharge, while the moment at which the voltage suddenly drops with the iron electrode, can be changed within certain limits by the method of preparing the active iron material; in general this point occurs in the discharge curve of the iron

electrode at an earlier and therefore more unfavorable phase of the discharge.

The curve showing the change of weight is nearly a straight line, if we neglect the small variations from the straight line at the beginning of the discharge. After thirteen ampere-hours have been given out by the cell, the direction of the straight line is changed somewhat. This moment corresponds to the new reaction which has now started in the active iron material. The increase of weight per ampere-hour is 0.44 gram for the first portion of the discharge curve and somewhat smaller for the second portion.

This simple experiment shows that the process at the iron electrode during discharge cannot be simply a combination of the active material with oxygen since it would then evidently be difficult to understand why the active material should undergo a contraction due to the addition of oxygen. An easier explanation of the contraction of the active iron material would be found in the assumption that the active material at the beginning of the charge is a hydrate, say of the formula,



If the process at the iron electrode during discharge would be simply oxidation, the increase of the absolute weight of the iron electrode per ampere-hour would be 0.3 gram (oxygen) and exactly this increase should have been found in our weighing experiments, if the supposition was fulfilled that the concentration of the liquid in the pores is equal to that of the free external solution, and that the volume of the active iron material has not changed during the passage of the current. With the very small discharge current of 0.5 amperes we may be justified in assuming that the concentration of the liquid in the pores differs very little from that of the free solution outside of the pores between the two plates during the whole time of discharge; for this reason the excess of the increase of weight over that due to oxidation, as shown in Fig. 2, must be assumed to be due to a contraction

of the active mass. If the absolute weight of the active mass filled into the pockets, as well as its specific weight are known at the beginning and at the end of an experiment, and if the volume of plate as well as the concentration of the free electrolyte are given, it would be easy to calculate the change of volume numerically. For the electrodes of the lead accumulator I have made such calculations in my pamphlet on diffusion phenomena on lead electrodes, mentioned above.

The increase of weight which an electrode would undergo if no concentration changes are allowed to develop in the electrolyte in the pores during the passage of the current, may be determined in two ways. The first way is the method used in the above experiment, by discharging the cell with an exceedingly small current. The second method is to discharge the cell more quickly with a larger current and to observe the changes of weight during the passage of the current as well as after the discharge has been stopped. The diagrams thus obtained are of special interest and are suitable for an investigation of the diffusion phenomena in the interior of the plates.

With the first method, one measures the absolute change of weight of the solid electrode, plus the change of the loss of weight equal to the weight of displaced electrolyte, on account

of the changed volume of the active mass; on the other hand, the influence of concentration changes in the liquid in the pores (that is, the factor  $-(s_0 - s)$ , due to the different migration velocities of the K and OH ions) may be considered as so small that it can be neglected, since diffusion and convection have time to destroy all concentration changes which tend to develop.

With the second method, after completion of the discharge, the cell is left at rest in order to accomplish that all concentration differences, existing between the liquid in the pores and the external free liquid, are gradually destroyed by diffusion and convection. After this has taken place, the change of weight measured (compared with the weight at the beginning of the discharge) equals again the absolute change of weight of solid electrode, plus the change of the loss of weight, equal to the weight of the displaced liquid, caused by the changed volume of the active material.

It is thus possible to control the accuracy of one of the above two methods by means of the other, under the supposition that during one experiment no self-discharge nor any development of gas occurs at the electrode.

#### DISCHARGE OF THE IRON ELECTRODE WITH 15 AMPERES.

It is, indeed, possible to get a fairly good agreement between the results of both methods. The same electrode which was used in the experiment of Fig. 2, was then discharged with

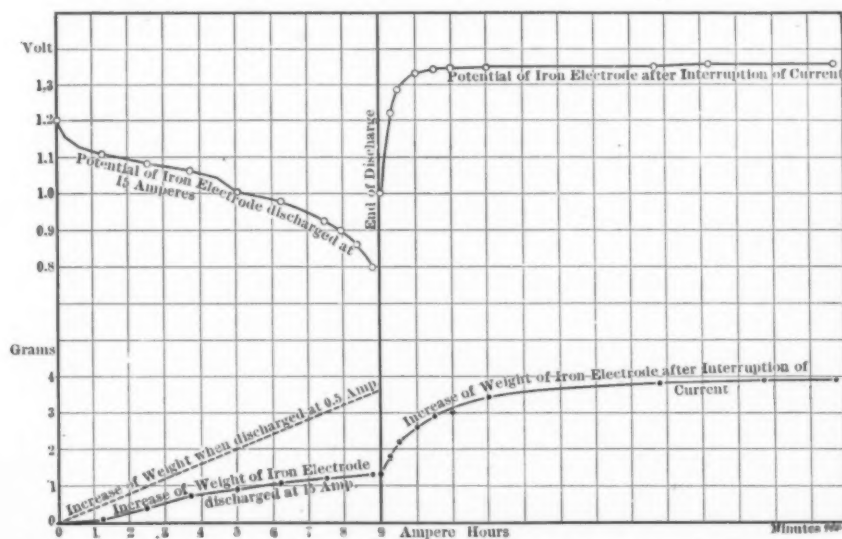


FIG. 3.—BEHAVIOR OF IRON ELECTRODE WITH HIGH DISCHARGE RATE (15 AMP.)

15 amperes, the results being given in Fig. 3. The average voltage at the terminals, which is of no special interest for our purpose, is, of course, much more unfavorable with this very high discharge rate than in the discharge with the thirty times smaller current (0.5 amperes of Fig. 2). The sudden voltage drop in the middle part of the discharge curve can still be seen, although it is less evident.

The curve of the change of weight has a shape which differs quantitatively from that in Fig. 2. It will be seen especially that the increase of weight is more than one-half smaller than in the former experiment.

It is improbable that the reactions taking place at the active materials of the plate are different from those in a slow discharge. The reason of the difference in the weight curves is, therefore, to be found in the different diffusion of the electrolyte under the different conditions of the two experiments. In other words, such diagrams show us the phenomena of diffusion at the electrodes at different discharge rates.

As will be seen from the above equations, the electrolyte in the pores of the iron electrode becomes more dilute on account of the formation of water during discharge, while the electrolyte in the pores of the nickel electrode becomes more concentrated since water here disappears. Other things being equal, the concentration change will be the greater the higher the rate of discharge or charge, *i. e.*, the shorter the time in which diffusion and convection are able to counteract the concentration differences developing on account of the electrochemical action. It is thus evident that the higher the discharge rate, the better should be the agreement between the observed concentration changes in the liquid in the pores, and those calculated by Roeber's method.

If, at the end of discharge, the circuit is broken, diffusion and convection will begin to annihilate the concentration differences between the dilute solution in the pores of the iron electrode and the external, more concentrated solution. The iron electrode must therefore increase in weight until there are no longer any concentration differences.

A small increase of weight of the suspended iron electrode after the interruption of the current is observed even after the discharge with the low rate of 0.5 amperes (Fig. 2). The increase in weight was 0.95 gram after the cell had been left at rest for thirty-six hours, and simultaneously the *e. m. f.* increased to 1.145 volts.

Much more significant are the results obtained in the experiment with the high discharge rate of 15 amperes. After the current has been interrupted, the external electrolyte which had a specific gravity of about 1.25 in all experiments, diffuses vehemently into the pores of the plate and raises the concentration of the greatly diluted solution in the pores. The result is that the weight of the electrode, while left at rest, first increases rapidly and afterwards more slowly; after four hours the increase of weight is 2.6 grams, so that the total increase of weight for the 8.7 ampere hours taken out of the plate, is  $1.3 + 2.6 = 3.9$  grams. With a discharge rate of 0.5 amperes the corresponding value for the same number of ampere hours was 3.8 grams.

The well-known phenomenon of the *e. m. f.* of a lead accumulator rising again,

when left at rest after a discharge at a high rate, has been shown by Dolezelak to be simply due to diffusion of the acid; the *e. m. f.* increases until there is no longer any diffusion of acid between the electrolyte in the pores and the outside electrolyte. With a lead peroxide plate (where the *e. m. f.* is in linear relation to the acid concentration) it is thus possible to use the curve showing the diffusion while the cell is at rest, in order to conclude from it correctly what the simultaneous changes of the *e. m. f.* are.

In Fig. 3 the change of the *e. m. f.* in the time, after the circuit has been opened, after completion of the discharge with 15 amperes, is shown in the upper right hand part of the diagram. The curve first rises rapidly and assumes after one hour the value of 1.35 volts and changes in the next three hours only very slightly, namely, by 0.01 volt only.

No exact measurements have yet been made on the relation between the concentration of the electrolyte and the *e. m. f.* But from those observations which I have made I would conclude that for equal porosity of the active materials, the iron

electrode is somewhat more capable of regaining its potential, when left at rest, than the nickel electrode. It is very probable that in the nickel electrode the temperature changes of the electrolyte are of much greater importance than concentration changes, and therefore the nickel-iron accumulator will probably have a higher temperature coefficient than its old rival.

The results of weighings of a cadmium electrode of the same size as the iron electrode discussed before, are given in Fig. 4. The voltage and weight curves are not essentially

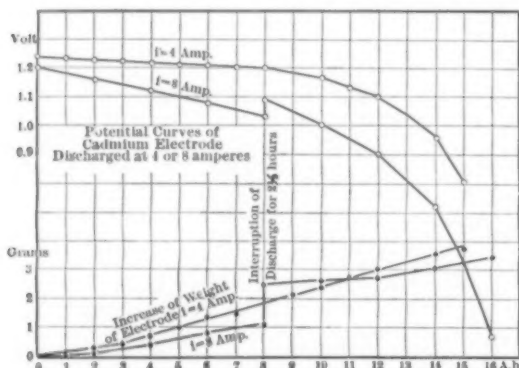


FIG. 4.—BEHAVIOR OF CADMIUM ELECTRODE

different from those of the iron electrode, but the relation between discharge rate and change of weight is more evident than with the iron electrode. A so-called "double voltage" is not observed with the cadmium electrode.

(To be concluded in our next issue.)

#### GERMAN BUNSEN SOCIETY.

REPORT OF THE NINTH GENERAL MEETING IN BONN.

BY H. DANNEEL, PH. D.

The ninth general meeting of the German Bunsen Society for Applied Physical Chemistry (formerly the German Electrochemical Society) was held in Bonn on May 13th and 14th. There were, in the whole, 150 members and guests present, among them numerous official delegates of institutions and of German and foreign societies. Prof. Roscoe, Prof. Landolt and Prof. Ramsay were elected honorary members. The next general meeting will be held in Karlsruhe in the week following Whitsunday, 1905.

#### MEETING OF MAY 13.

The papers presented at the first session dealt mainly with various scientific questions involved in iron metallurgy.

#### THE APPLICATION OF THE PHASE RULE TO ALLOYS OF IRON AND CARBON.

A paper on this subject was presented by Prof. BAKHIUS ROOZEBOOM, of Amsterdam. The solidification of iron, containing carbon, and the simultaneous formation of iron-carbon compounds are of special importance for the metallurgy of steel. Attempts to explain these phenomena on the basis of the phase rule were first made in 1896. Since that time the researches of various investigators have led to the development of very concise ideas concerning these phenomena. The author gave a diagram showing the changes with temperature of alloys of iron and carbon, with temperatures varying between 1500° and 500° C., and for alloys containing various proportions of carbon, between 0 and 8 per cent.<sup>1</sup> The author

<sup>1</sup> In all essential points this diagram is the same as that given in Dr. W. Campbell's article, on page 49 of our February issue, 1904. It is, therefore, not reproduced here.—Ed.

also exhibited a number of other diagrams concerning which, however, our knowledge is not yet complete in all details. A question not yet decided,<sup>2</sup> is whether cementite ( $\text{Fe}_3\text{C}$ ) is stable at higher temperatures; according to the author, it seems that cementite is unstable at all temperatures.

#### HARDENING STEEL BY SUDDEN COOLING.

Prof. HEYN presented a paper on the compounds of Fe and C, which are formed when steel is hardened by sudden cooling. An eutectic mixture remains unchanged; otherwise non-homogeneous mixtures of ferrite, cementite, pearlite, troostite, etc., are formed. Troostite is formed especially if the velocity of cooling is small. If manganese is present, the formation of troostite is greatly counteracted. The author exhibited a great many lantern slides showing clearly the structure containing the various Fe—C compounds.

#### MANUFACTURE OF CALCIUM.

In a paper on this subject, Dr. RATHENAU first gave an historical review of the methods devised for winning calcium. It was first made as amalgam. Bunsen precipitated it from a saturated  $\text{CaCl}_2$  solution, Mathiessen from salt mixtures and Borchers<sup>3</sup> produced it in spongy form by electrolysis of fused  $\text{CaCl}_2$ . The author stated that the efficiency of the Borchers process is not high and his calcium has a purity of 90 per cent only.

Suther and Redlich have worked out a new electrolytic method in the laboratory of the Allgemeine Elektrizitäts Gesellschaft. The feature of their method is that the cathode is made to just touch the surface of the fused calcium chloride; it is gradually raised during operation in such a way that the calcium deposited at the end of the cathode remains just in contact with the fused bath. Calcium rods are thus obtained of 3 to 4 cm. diameter and 20 to 30 cm. length.

Replying to a question of Prof. Van't Hoff, whether it would pay to make Al—Ca alloys, Dr. Rathenau replied that these can be obtained only in small quantities. Muthmann stated that it is quite easy to produce calcium from a mixture of two thirds of  $\text{CaCl}_2$  and one-third  $\text{CaF}_2$ .

#### DISSOCIATION PHENOMENA AT HIGH TEMPERATURES.

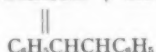
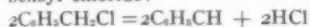
In a paper on this subject Dr. LOEB remarked that the condition which must be fulfilled to start a chemical reaction, is the presence of free valencies. Dissociation may be considered as a process by which substances in which many of the valencies are saturated, are changed into constituents in which only a small portion of the valencies is saturated. From this point of view, dissociation must exist, to enable any chemical reaction to start. Electrolytic dissociation is only a special case, the peculiar feature of which is that the concentration of the products of dissociation, i. e., the ions, is very great. This is the reason why ions react with a much greater velocity than the parts which are formed by dissociation of organic substances. The supposition that all substances are always dissociated (although only a small part of the same may be dissociated) is a good means for explaining reactions of organic chemistry.

To study the phenomena of dissociation the author heats the substances in a glass vessel which is provided with a refrigerator, and in which a platinum wire is heated electrically. In general it is not possible to detect the real products of dissociation, since they are stable for a short time only. But it is often possible to conclude what they are, from the final products. For instance, benzene changes at high temperatures diphenyl and  $\text{H}_2$ , and the process must be assumed to be  $\text{C}_6\text{H}_6 = \text{C}_6\text{H}_5 + \text{H}$ . Afterwards  $\text{C}_6\text{H}_5$  and H form diphenyl and hydrogen molecules. In this way the author gave the theory of the decomposition of chloroform, chloral, benzyl chloride, benzal chloride, and benzotrichloride. As an ex-

<sup>2</sup> ELECTROCHEMICAL INDUSTRY, Vol. I. (1902-1903), page 104; see also page 143 and 122.



ample, may be given his scheme of the decomposition of benzyl chloride:



In all these reactions, the starting materials which contain four-valent carbon change into substances with carbon of a lower valency, but these are unstable and, therefore, form new and more saturated complex compounds. One must assume that the intermediary products can exist for a short time; under certain conditions it is possible to obtain them, for instance, CO, methyl, triphenyl, etc.

The author believes that valency is a function of the conditions of the experiment, for instance, a function of pressure, temperature and the medium in which the reaction takes place. High temperatures decrease the number of valencies, for instance, at high temperatures a mixture of HCl and  $NH_3$  is not capable of reaction, since the free valencies required for the reaction are missing. If the temperature is increased, or if the substances are brought into a suitable medium, or if the pressure is increased, new valencies are formed and  $NH_4Cl$  is formed. The substances assume the maximum number of valencies at an absolute temperature zero.

#### COLLOIDS.

In a paper on this subject, Dr. E. JORDIS expressed the opinion that the theories that have so far been offered on colloids are wrong. He has fitted up for himself the following scheme. Electrolytes, which, with proper additions, are capable of forming colloids, are in a special state, in a certain intermediary state which is specially suitable for the change into a colloid. The formation of colloids is only possible, if at the same time impurities are present. This is true also for the colloidal metal solutions of Bredig because the distilled water always contains dust, gases and impurities. All colloids are amphoteric, so as to react as well with acids as with alkalis. If the affinity with acid is greater, the liquid becomes alkaline. Colloids are not essentially, but only gradually different from crystalloids. According to the conditions of the experiment, the colloids may travel either towards the anode or the cathode under the influence of the electric current.

#### PASSIVITY OF METALS.

Dr. WOLF JOHANNES MUELLER stated that there are two theories for the explanation of the passive state of metals. One theory assumes that an oxide film is formed on the metal, the other that the metal itself assumes a new condition. There are certain points which speak against the first theory. For instance, iron reflects in air 60 per cent of the light; this reflection is not changed when the iron assumes the passive state, so that no optically active oxide layer can be present. The author tries to explain the passive state by the electronic theory. According to Riecke and Drude, there exists in a metal always a dissociation into positively charged metal atoms and into negative electrons. An equilibrium exists between both. On account of the great affinity of the metal to the positive electrons, only the negative electrons are capable of free movement, and for this reason the transport of electricity through a metal is accomplished by the negative electrons only.

If a metal is used as anode, positive electrons pass into the solution, either in form of ions or in form of positive electrons; in the latter case the electrolyte is oxidized. Whether the one or the other phenomenon takes place, is determined by the force with which the positive electrons are held by the metallic atoms. This force is measured by the potential of the electrode, and, according to Hittorf, it is the smaller, the greater the valency with which the metal passes into solution. If this force is very small, the metal does no longer pass into solution at all; in other words, it is in the passive state. If a metal assumes the passive state as anode it is because it assumes a

higher valency; for this reason only such metals can assume the passive state which can assume different valencies.

At the anode there is a large potential drop because the metal with its high conductivity is in contact with the electrolyte with its smaller conductivity. Negative electrons are there sucked out, and the condition of electric neutrality is maintained by positive electrons passing into the solution. This is the easier the higher the valency with which the metal passes into solution. We may say that by the negative electrons passing away, the dissociation in the metal is increased so that the metallic atoms assume more positive charges. The reverse phenomenon is found at the cathode. There the negative electrons arrive and decrease the dissociation: metal = positive metallic atoms + negative electrons, and the metal assumes its lowest valency. If a cathodically polarized metal is then again made anode it passes into solution with a lower valency, i. e., it has become active.

Metals also become passive by immersion in certain solutions, for instance, in  $HNO_3$ . The author explains this by local currents, which pass between the metal and the impurities present in every metal. The depolarizing property of the electrolyte decides whether the cathodic effect, producing activity, or the anodic effect, producing passivity, is greater. The phenomena of the passive state are very clearly exhibited by manganese. At a sufficiently high current density, 0.07 to 0.15 ampere per square centimeter, manganese in a slightly acidulated sodium phosphate solution passes into solution, with simultaneous development of oxygen. This produces considerable variations of the potential of the electrode.

There was considerable discussion of this paper. Bredig remarked that the argument brought forward by the author against the oxide film theory might not be decisive, since it is a question how thick a film must be to be optically active. To produce a chemical action the film can be very thin. A film of  $10^{-8}$  cm. is sufficient to completely change the chemical properties of the metal.

Owing to limitations of space the report of the other papers presented at the meeting is reserved for our next issue.

#### ADAPTABILITY OF ARTIFICIAL GRAPHITE ARTICLES.

By C. L. COLLINS, 2D, E. E.

Graphite articles manufactured by the Acheson process need no introduction. The principal characteristics are great purity, high electrical conductivity, lubricating properties, and resistance to oxidizing and disintegrating action. They are manufactured in a manner which avoids the use of the hard vitrified clay bonds usually associated with graphite articles. Being pure graphite with all the characteristics of this form of carbon, they can be cut or machined with the greatest ease and at slight expense. Some of the possibilities of this feature were pointed out in a paper on "Graphite Electrodes in Electrometallurgical Processes," read before the American Electrochemical Society at their inaugural meeting in Philadelphia, April 4, 1902, and again briefly in an article on "Graphite Electrodes in Electrolytic Work," which appeared in *ELECTROCHEMICAL INDUSTRY*, September, 1902. It will doubtless interest electrochemists to know what has actually been accomplished in this connection in regular commercial work, and with this end in view the following data, including some figures covering exact costs, have been collected.

A method of using electrodes for electric furnace work, so that no waste occurs, is shown in Fig. 1. This represents an old elec-



FIG. 1.—JOINTING FURNACE ELECTRODES.

trode, or stub *c*, which, while in use was consumed as close to the metal holder *a* as permissible. A new electrode *b* is then joined to *a*, and *c* in turn connected to *b*. Heretofore the part *c* has been wasted.

The form of threaded joint used is given a slight taper, which, with the graphite electrodes, gives the maximum strength. The two adjoining shoulders should be faced so as to make a tight fit. The metal holder *a* is also given a slight taper at the outer surface, and by a form of clamp the whole is supported over the surface from above. This ring *a*,



FIG. 2.—ELECTRODES USED IN ACKER PROCESS FOR ELECTROLYZING FUSED SODIUM CHLORIDE.

which is of brass, and the supports from above also act as the conductors to the graphite electrodes. By this method the furnace must be shut down for electrode renewals, but in the process in question this is not objectionable as the furnace is shut down in any case at certain definite intervals to remove the charge. It is evident, however, that by a slight modification a new electrode could be joined to the end of one in use, and these fed into the furnace continuously as consumed.

In order that some idea may be gained of the practicability of this method, it may be mentioned that in one process over a carload of graphite electrodes per month is being machined and joined in this manner without waste. The cost of machining both ends of an electrode 6 inches in diameter, is about fifty cents per electrode, and for an 8-inch electrode, about sixty cents, which includes actual labor, cost of tool steel and repairs. In either case about 3 inches of the electrode length is sacrificed costing fifty-nine cents for the 6-inch and ninety-seven cents for the 8-inch. Thus the total cost of a male and female joint is \$1.09 for the 6-inch and \$1.57 for the 8-inch, or about 11½ and 10 per cent, respectively, of the cost of the electrodes themselves in lengths of 48 inches.

The method is especially applicable for electric furnace processes in the manufacture of ferro-alloys or where very heavy current and the concentration of the energy in a small space are desired. With electrodes 8 inches in diameter over 5,000 amperes may be used without apparent resistance or heating at the joints and with 6 inches from 3,000 to 4,500 amperes. One electrochemist has even used 7,500 amperes in a jointed 6-inch graphite electrode for certain work without difficulty. With a 6-inch amorphous carbon electrode not more than 1,500 amperes could be carried efficiently.



FIG. 3.—ELECTRODE USED IN RHODIN PROCESS FOR ELECTROLYSIS OF SODIUM CHLORIDE SOLUTION.

Another manufacturer in electrometallurgical work, by using large assembled terminals consisting of a specific form of electrode holder and a peculiar arrangement of several graphite electrodes, has effected a saving in the electrode cost per ton of output in his furnace of approximately 20 per cent. This is in comparison with former methods when amorphous carbons were employed and takes into account not only the cost of the electrodes, but also that of the repair fittings, labor of assembling, placing in the furnace, etc. The comparative tests were very thorough, extending over several years, and

represent a consumption of several hundred thousand pounds of electrodes per annum.

The cost of threading the graphite electrodes in this case amounts to only fifteen-hundredths of a cent per pound of electrodes. In using graphite only 132 pounds per terminal is necessary, on account of its high electrical conductivity, as against 352 pounds for the amorphous carbon. There is little difference in the cost of fitting and assembling, and, as the graphite costs more per pound, the total investment per terminal is practically the same in either case. The saving is, therefore, due to a longer life and consequently fewer numbers of electrodes to be handled, but is also due to the ease of handling and consequent saving in labor. A further and very important factor is the *greater uniformity of the graphite article*. Special stress is laid on this latter point, for the former high cost of the amorphous carbons was principally due to the fact that the average life of these articles was

considerably below the maximum, whereas with the graphite electrode there is practically no variation and definite results can be expected. It is of the utmost importance that a furnace run does not have to be interrupted to renew electrodes before the operation is complete. A further factor in the saving is the fact that the stubs of the graphite electrodes are not wasted, but can be joined and used as new electrodes by a simple form of threaded joint.

The style of anode used in the Acker process for the manufacture of chlorine and caustic soda with a fused electrolyte and a fused lead cathode is well known, and is shown in Fig. 2. The working anode proper is the lower face of the block *a*, which is grooved and rounded to allow of the ready escape of the anode gases. A number of these blocks are arranged side by side in each cell. Two graphite rods *b*, each 5 inches in diameter, are threaded into the upper face of *a*

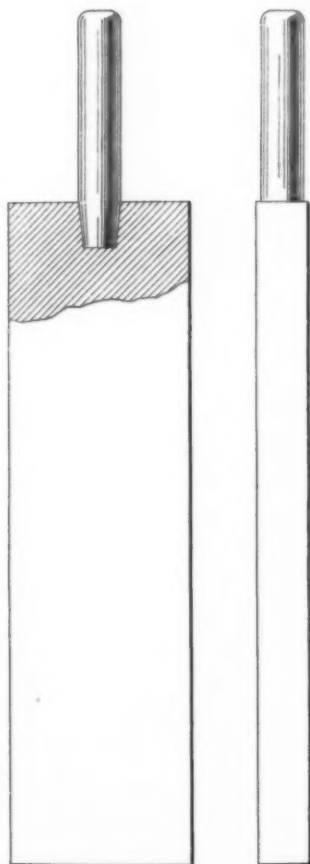


FIG. 4.—SIMPLE ANODE FOR ELECTROLYTIC WORK.

and act as the leading-in conductors from the metal terminal *c*. These terminals are cast-iron caps screwed over the tops of the rods *b* and cross-connected by heavy brass bars, to which the circuit is finally connected. The graphite rods *b* are encased in tile pipes to protect them from oxidation, which would otherwise take place slowly at the working temperature of the cell. The spaces between the metal caps and the upper edges of the tile pipes are made air-tight by thoroughly cementing with a suitable fire-clay mixture, which is afterwards baked. Each anode block carries a working current of 2250 amperes. The cost of threading both ends of each round electrode is only three cents, and the cost of drilling, tapping and corrugating the block, eleven cents, or a total cost for the

machine work upon the graphite of only seventeen cents per anode. The advantage of this form lies principally in the saving resulting from the high electrical conductivity of the graphite electrodes and the use of the minimum possible electrode material for conducting the current from the metal caps to the anode block *a*.



FIG. 5.—ANODE USED IN McDONALD DIAPHRAGM CELL.

In Rhodin's process the cell is circular in form, and is divided into a number of segmental compartments, in each of which is a graphite anode of special design. One of these anodes, of which there are six per cell, is shown in Fig. 3. It consists of a triangular graphite block *a*, which also acts as the cover and fits tightly in its anode compartment. Through the block *a* a number of 1¼-inch graphite rods *c* are threaded. The threading allows these to be lowered as they disintegrate at the ends. The total current used per anode is about 150 amperes, and is conducted to the block by a 2-inch graphite leading-in rod *c*. The cost of drilling and tapping the block and threading the rods is about \$2.25 per anode.

A simpler form of anode for electrolytic work is shown in Fig. 4. This illustrates one of the fundamental principles in graphite electrode work, viz., the use of a leading-in rod designed to utilize the high electrical conductivity of graphite and a working slab designed to give the maximum surface for its weight and still be of sufficient thickness to allow for disintegration. In this case a rod 1½ inches in diameter x 9 inches in length, carrying a current of 46 amperes, is used in connection with a 2 x 7 x 25 inch slab. Only one side of the slab is used as working face, the anode being turned, exposing a fresh face, when seriously corroded.

A rod 1½ inches in diameter has also been used to carry 58 amperes without appreciable drop. A very simple taper joint is used and gives no trouble. With proper tools a very few minutes suffices to ream the hole and taper the rod, and as it is done by the man tending the cells, it practically adds nothing to the cost. In any case it is more than offset by the saving in electrode weight.

The saving in graphite, however, is not the only advantage which is realized from this form of anode, inasmuch as the holes through the covers of the cell are much smaller and easier then to pack, if the entire cross-section of the anode slab were brought through the cover. As these anodes are near together the construction of the cover itself is simplified by the avoidance of narrow sections. Five inches would have to be added to the length of the anode slab if the rod connection could not be used.

In Fig. 5 a similar form is shown, a ¾-inch lead rod being used in place of graphite. The lead rod is screwed into a 4 x 4 x 14 inch graphite block, the total current carried being 60 amperes. All four sides act as working faces. The end of the graphite block, into which the lead rod is inserted, is boiled in paraffine and gives no trouble due to corrosion at the contact. In all future work, however, a graphite rod 1½ inches in diameter is to replace the lead conductor. This form is used in the McDonald diaphragm process, both in the manufacture of bleaching powder and caustic soda, and in the chlorination of gold ores.

The illustrations given above all relate to the use of graphite articles in electrochemical processes. In such work graphite

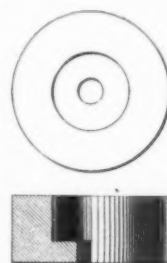


FIG. 6.—GRAPHITE BUSHING.



is used not solely on account of its adaptability, but because of other valuable properties, such as purity, high electrical conductivity and resistance to oxidizing and disintegrating action. A more striking illustration, however, of the use of graphite on account of its adaptability, or the ease of machining, is shown by the bushings in Fig. 6. These bushings are about one-half inch in diameter and are used in connection with rheostat work. Five thousand of these bushings were made up from solid graphite rods on a screw machine by a boy in twenty-seven hours without a single defective piece. The cost was one-tenth cent for the machining, and one-tenth cent for the graphite, or a total cost of two-tenths cent per bushing. As far as the requirements of the work are concerned, amorphous carbon bushings would be equally satisfactory, but amorphous carbon bushings of the size and shape shown which must necessarily be molded articles, cost from two and one-half to three cents per piece.

A similar saving can be effected in the case of the small plungers used in dash pots in connection with arc lamps and circuit breaker time relays. We know of one case where small molded graphite plungers were being supplied at \$6.00 per dozen corresponding to about \$15.00 per pound. Graphite plungers machined to the same size from solid rods cost about fifty cents per pound.

The contacts used in circuit breakers are usually of some irregular shape and are clamped tightly in holders of similar section. For this purpose either molded carbon or machined graphite is satisfactory, the latter having the higher conductivity. The graphite contacts, however, possess other decided advantages, such as non-arcing properties, which characteristic is of considerable value where a circuit is interrupted constantly, and where the current has some magnitude.

In conclusion it may simply be said that the use of graphite articles is not limited to the electrochemical field nor to work requiring articles of high electrical conductivity, purity, resistance to oxidizing and disintegrating action, and lubricating properties. Its sphere of usefulness embraces all the lines of work in which the ordinary forms of carbon have heretofore been used. It is generally more satisfactory than carbon, and in some cases very much less expensive. Users of any form of molded carbon articles can profitably investigate the cost of similar graphite articles.

#### ELECTROMETALLURGY OF IRON AND STEEL

In the metallurgy of iron and steel the use of the electric furnace has so far been mainly successful on a commercial scale for the solution of two special problems. The one is the manufacture of ferro-alloys, the other the production of special steels. For the production of ferro-alloys it is the ease of producing very high temperatures by means of the electric furnace which has made its application preferable and in some cases necessary, on account of the high temperature of reduction of the oxides (of titanium, etc.) to be reduced. On the other hand, the features which render the electric furnace very suitable for the manufacture of special steels, are the ease of control, the cleanliness of operation, and the absolute prevention of impurities being introduced into the charge from furnace gases. However, these are not the only problems in which electrochemists have tried to introduce the electric furnace in the iron and steel industry. The big problem—that of the reduction of iron ores and the manufacture of iron and steel from the ores—has repeatedly been attacked, although no process of this kind has so far been able to prove its practicability on a large commercial scale.

A great amount of such pioneer work has been done in Europe. The reason is a peculiar one which has really nothing to do with iron and steel. When some years ago it was found that calcium carbide could be easily made in the electric furnace and that by means of the simple reaction of calcium carbide with water, it was possible to get acetylene,

promising to be of great importance for the lighting industry, there was started a great boom, and wherever there was a water-power a calcium carbide plant was erected in Europe. It must be understood that the calcium carbide industry in Europe is not in the hands of a single company, as it is in this country. The result was over-production, a collapse of prices and a serious crisis in the calcium carbide industry of Europe. The question was now what to do with electric furnace plants which had been erected and in this crisis nothing seems to have attracted the attention of the European electrometallurgical engineers to a greater degree than the possibilities of electric furnace processes in the iron and steel industries. In former issues we have described in detail nearly all the more important attempts which have been made in this direction.

The matter has become of great actual importance in this country on account of the interest which the Canadian Government has taken in this matter, with a view of introducing an electric iron and steel process on a large scale in Canada where large water-powers and cheap iron ores are available. We have already noticed (page 48 and 198 of this volume) that a commission, appointed by the Canadian Government, and headed by Dr. Eugene Haanel, was sent to Europe to investigate the different electric furnace processes in question, and that the committee has recently returned, convinced that its trip had been entirely successful.

A summary of the main facts ascertained by the committee and embodied in its report to the Canadian Government has recently been given in the "Canadian Manufacturer" from which we take the following passages. For a description of the Keller furnace which takes such a prominent place in the report of the commission, we may refer our readers to an article by Mr. Bennie in our January issue, 1903, page 162.

#### KELLER FURNACE.

By far the most important experiments witnessed by the commission were those made by Mr. Keller, of Keller, Leleux & Co. in Livet, France. Some 90 tons of iron ore were used to show the economic production of pig iron by the electric process. The furnaces employed for these experiments were the furnaces used in the regular work of the company for making the various ferro-alloys, such as ferro-silicon, ferro-chrome, etc. The company at the time of the visit of the commission were under contract to furnish ferro-silicon to the Russian Government, but generously interrupted their pressing regular work to undertake the making of experiments for the commission. The furnace employed is of the resistance type, and consists of two iron castings of square cross-section, forming two shafts communicating with each other at their lower end by means of a lateral canal. The cases are lined with refractory material. The base of each shaft is formed by a carbon block. These blocks are in electric communication on the exterior of the furnace by means of copper bars. The carbon electrodes to which electric current is distributed pass two-thirds of their length into the shaft. The electrodes are prisms 72 cm. (28 inches) in diameter and 135 cm. (53 inches) long. Three sets of experiments were made, as follows: 1. Electric reduction of iron ore and obtaining different classes of pig, gray, white and mottled. 2. Electric reduction of iron ore containing a definite amount of carbon in the charge, with a view of ascertaining the amount of electric energy absorbed in the production of 1 ton of pig iron. 3. The manufacture of ordinary steel of good quality from the pig manufactured in the preceding experiments.

The different classes of pig iron were obtained without difficulty, and the furnaces throughout the experiments worked quietly and without the slightest accident, the gas discharging on top in flickering flames, showing that the gas resulting from the reduction of the ore escaped at low pressure. The workmen employed were ordinary Italian laborers without any special training. A number of castings, such as columns,

pulleys, gear wheels, plates, &c., were made, the metal drawn directly from the furnace. The castings showed sharp edges, a comparatively smooth surface, and were sound throughout.

For the determination of the electric energy absorbed, the voltmeter and ammeter employed to measure the volts and amperes were calibrated in the laboratory of the director of the electrical department of the University of Grenoble, who also ascertained the power factor of the alternator furnishing the electric energy. The electric energy absorbed per ton of pig was found to be 0.226 horse-power year.

#### COST OF PROCESS.

1. Ore (hematite metallic iron 55 per cent, 1,842 tons at \$1.50 per ton .....	\$2.76
2. Coke for reduction, 0.33 tons at \$7 per ton .....	2.31
3. Consumption of electrodes at \$5 per 220 pounds ..	0.77
4. Lime .....	0.30
5. Electric energy, 0.226 horse-power year at \$10 per each horse-power year .....	2.26
6. Labor at \$1.50 per day .....	0.90
7. Different materials .....	0.20
8. General expenses .....	0.40
9. Repairs maintenance, etc. ....	0.20
10. Amortization (machinery and buildings) .....	0.50

Total, exclusive of royalty .....

To satisfy the commission, Mr. Keller made experiments to illustrate his process of making steel. The details of the operation and the figures relating to his experiments are in the hands of Prof. Harbord, the English metallurgist, who accompanied the commission.

In regard to other processes it was found that Mr. Harmet of St. Etienne, who published papers and obtained patents on the electric process for smelting iron and making steel and Mr. Gin of Paris, who has obtained a patent for the production of steel from scrap, have as yet no plant in operation by which their methods might be tested.

#### PROSPECTS OF THE ELECTRIC FURNACE.

In his general conclusion, Dr. Haanel says: "It must be pointed out that the results obtained at Livet were the results of experiments in furnaces not specially adapted to the work required to be done. With the improved furnaces of which the commission has secured detailed drawings, permitting on account of higher column of charge a more effective use of the reducing power of the carbon monoxide evolved, and the employment of machinery for charging the furnace to reduce the cost of labor, a much better figure than the one given will result."

The processes of electric smelting must yet be regarded as in the experimental stage, no plant existing at present where iron ore is commercially reduced to pig by the electric process. The more remarkable therefore it appears that experiments made off hand, so to say, in furnaces not at all designed to be used for the production of pig, should give a figure of cost which would enable an electric plant properly designed and managed to compete with the blast furnace. It is, moreover, reasonable to expect that, as experience in electric smelting accumulates, the design of the electric furnace best suited to the conditions of the high temperatures with which the metallurgist has to deal will undergo changes which will reduce the absorption of electric energy to a minimum. The electric engineer will also be called upon by the new industry to design electric plants specially suited to the conditions of electric smelting.

When it is considered that the electric process is applicable to the smelting of all other ores, such as copper, nickel, silver, etc., that the furnaces are of simple construction and the regulation of the heat supply is under perfect control, we may expect that the application of electric energy to the extraction of metals from their ores will not be long delayed, and that familiarity with handling large currents, and experience

gained in electric smelting will result in displacing some of the costly and complicated methods by comparatively simple and economic processes. The immediate effect of a plant erected for the smelting of iron ores which will demonstrate the economic production of pig and the making of steel will arouse the faith of the industrial world in the new metallurgy, and other industries dependent upon electricity as the agent or to which electricity can be applied will follow as a consequence in the wake of this power plant.

#### MANUFACTURE OF SPECIAL STEELS.

At Gysinge, Sweden, steel of superior quality is made by the smelting together of charcoal, pig and scrap in an electric furnace of the induction type—that is to say, a furnace without electrodes. This process corresponds to the crucible steel process, but it has certain advantages over the latter in that the melted materials at no time during the operation are exposed to gases, some of which when absorbed deleteriously affect the quality of the product. The furnace worked quietly and regularly, producing on the average 4 tons of steel in twenty-four hours. Tapping occurring every six hours, 0.116 electric horse-power years were required per ton of product. The cost at the rate of \$10 per electric horse-power a year would be \$1.16 per ton of product. At Korfors, Sweden, the Heroult process of making steel is in operation, but the furnace is at present employed in the making of ferro-silicon.

At Lapras, France, steel is also made from melted scrap. The process differs from that at Gysinge, in that it permits of the purification of the materials employed, two slags being made for that purpose, and carburization is effected in the furnace by carbon briquettes. The furnace is of the tilting pattern, consisting of an iron casing lined with dolomite brick. The bottom of the furnace is filled on top of the lining with crushed dolomite, upon which the charge reposes. Two electrodes pass through water-cooled joints in the roof of the furnace. The electrodes are vertical and parallel, and are adjusted vertically either by hand or a specially constructed regulator. An alternating current of 4000 amperes of 110 volts is distributed to the electrodes. Different classes of steel are made by the company at a cost per electric energy absorbed of \$1.54 per ton of ingot. The selling price of the steel varies from 363 francs 60 centimes to 123 francs 60 centimes per ton, depending upon quality.

Interesting experiments were made for the commission at this plant in the production of pig from the ore in a very simple furnace consisting of an iron box of rectangular cross sections, open on top and lined with refractory material. The bottom of the furnace in communication with the iron casing constituted one terminal of the electric circuit. A carbon electrode of square cross-section and about 3 feet in length, placed vertically in the open top of the furnace, constituted the other terminal. By hand regulation this electrode could be lowered or raised within the furnace. Thirty charges of ore were made during the working, and thirteen taps of metal and slag were taken.

#### MEETING OF THE FARADAY SOCIETY.

An ordinary meeting of the Faraday Society was held on June 9, the president, Dr. J. W. Swan, being in the chair.

M. Adolphe Minet presented the first part of a paper on the electric furnace; its origin, transformations and applications. The paper discusses the growth of the furnace from the historical point of view, and then proposes a new classification which is worked out in minute detail in the form of a table. A full bibliography of the electric furnace completes this section of the paper. The discussion was postponed until the autumn, when the author will complete his study and fully illustrate his subject.

Dr. F. M. Perkin described a form of porous diaphragm which he has found convenient for laboratory use. It consists of two perforated concentric porcelain cylinders packed

in between with brown paper, asbestos, or other material, depending on the use to which the diaphragm is to be put.

Mr. G. T. Beilby read a paper on the hard and soft states in metals. The wide range of the phenomena which are directly or indirectly associated with the hard and soft states in metals indicates that a knowledge of these states is of fundamental importance. An exclusively crystalline theory of metal structure, even when stretched to its widest limits, is insufficient to fully explain these phenomena. But the crystalline is not the only form of solid aggregate; the movement of the molecules in the liquid state may be so suddenly arrested that they have no time to fall into the regular formation of the crystalline state, so that the solid which results is amorphous, not crystalline. A suddenly congealed liquid may be likened to an instantaneous photograph of the rapidly moving molecules of the liquid state.

The views advanced were based on the author's earlier observations on surface flow in crystalline solids. The evidence afforded by the micro-structure has been supplemented by observations on the other properties of metals in the hard and soft states, and the view was now advanced that these states are perfectly distinct phases. This is shown by the mechanical, electrical, optical, and thermo-chemical properties, as well as by the micro-structure. The soft phase is crystalline and the hard phase is amorphous.

The transformation of hard into soft is effected by heat and takes place at a definite transition temperature. On either side of the transition point the various properties are characteristic and distinct; for instance, an e. m. f. of 120 microvolts may be developed in a thermo-junction of silver in the two phases. The e. m. f. falls to zero after the junction has

been heated to 260° for a few seconds. Silver leaf, which is opaque and highly reflecting below the transition temperature, becomes transparent and very much less reflecting if kept for a time at a temperature a little above the point.

The transformation from hard to soft is thermally irreversible, but is readily effected mechanically. The reverse transformation—soft to hard—takes place when the metal is deformed by overstrain, however slight. It takes place through an intermediate mobile phase in which the molecules have a freedom analogous to that in the liquid phase. This freedom is produced by motion directly imparted to the molecules during the slipping of one portion of the material over another. The state of the mobile phase is somewhat analogous to that of an undercooled liquid. This transformation, soft-intermediate-hard, while it occurs at every moving surface, does so as a rule in extremely thin layers. The layers of the hard phase, which result supply a rigid casing for the unaltered crystalline elements, and thereby give a granular and cellular structure to metal which has been overstrained by having any kind of work done on it. The co-existence of the two phases in this way accounts for the variety of structure which may be developed in malleable and ductile metals.

In the discussion of the paper, Dr. T. M. Lowry said that the temperature which Mr. Beilby called the transition point, was not a true transition point, such as exists, for example, in sulphur at 96° C., at which the rhombic passes into the monoclinic phase, but really the stability-limit; that is, the temperature at which the mobility of the molecules enables a change which has been trying to take place all along to do so at a visible velocity.

## ANALYSIS OF CURRENT ELECTROCHEMICAL PATENTS.

By GEORGE P. SCHOLL, PH. D.

### ELECTRIC FURNACES AND FURNACE PRODUCTS.

*Manufacture of Sulphide of Aluminium and Alloys of Aluminium.*—Miyagoro Onda, Nagoya, Japan. Patent 760, 554, May 24, 1904. Application filed October 14, 1903.

The first step of the process consists in comminuting the raw materials into a powder and mixing them intimately. These materials are: Oxide of aluminium, or ores containing it, charcoal, coke or other carbonaceous matter, and a metallic sulphide or sulphate, the heat of formation of which is lower than that of the corresponding aluminium salts. This mixture is formed into balls of pressure, after about five parts of its weight of coal tar have been added to increase its compactness. The balls are then baked in a retort and broken up again into pieces of the size of a bean. They are charged into an electric furnace, the walls of which are made of firebrick, while the bottom and the lining are formed of carbon. The latter constitutes one electrode, the other being formed by a hollow carbon rod, which passes centrally through the furnace cover. On both sides of the furnace there are receptacles, which communicate through a canal with the melting chamber of the furnace, one of them being intended for the reception of the melted aluminium alloy, and the other for the aluminium sulphide. An opening is provided for the escape of the gases, and the silicon sulphide formed in the reaction. The charge in the furnace is subjected to a temperature of about 2000° C., by producing an electric arc between the electrodes. The current density is 20 to 40 amperes per square inch of carbon rod, at 50 to 100 volts. When it is intended to produce an aluminium iron alloy containing, say, 10 per cent of aluminium, simultaneously with aluminium sulphide, the charge consists

of bauxite, 100 parts; charcoal, 40 parts, and sulphide of iron, 127.5 parts. The reactions are stated to take place as follows: The iron oxide is first reduced to metal by the carbon, while at the proper temperature the sulphide of iron interacts with

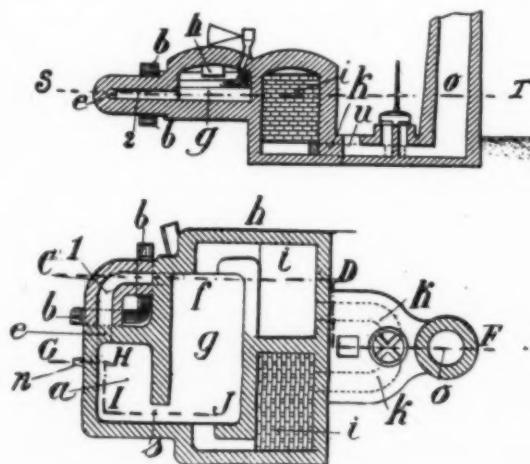


FIG. 1.—STEEL FURNACE.

the other ingredients after equation  $3\text{FeS} + \text{Al}_2\text{O}_3 + 3\text{C} = 3\text{Fe} + \text{Al}_2\text{S}_3 + 3\text{CO}$  and  $2\text{FeS} + \text{SiO}_2 + 2\text{C} = 2\text{Fe} + \text{SiS}_2 + 2\text{CO}$ . The silicon sulphide volatilizes, the iron greatly aids in the reduction of the alumina by the carbon, and an iron alu-



minium alloy is formed. The reason for using a hollow upper electrode is not disclosed by the inventor.

**Electric Furnace.**—C. P. E. Schneider, Le Creusot, France. Patent 761,920, June 7, 1904. Application filed October 12, 1903.

The furnace described in this specification belongs to the type of induction furnaces in which the electric current is produced by an alternating magnetic field. In the existing furnaces, which have annular crucibles of approximately uniform section, the great conductivity of the ring of molten metal is said to have resulted in the production of an extremely intense induced current, the reaction of which upon the primary coil produced an unfavorable phase displacement of the primary current. In the present invention the idea therefore has been to impart greater resistance to the molten metallic circuit by constructing it in the form of a tube of small cross-section which communicates at both ends with a chamber of large dimensions containing the greater part of the molten metal. This tube has sufficient inclination so as to insure an active circulation of the metal between the tube and the melting chamber, on account of the difference of density between the hotter and colder parts of the molten mass. The idea is shown embodied in various constructions. Its application to a multiple-chamber Siemens regenerative furnace for the production of steel is shown in Fig. 1 in plan and cross-section. Here *a* and *g* are the two furnace chambers filled with a bath of pig iron, into which the branches 1 and 2 of the V-shaped heating tube open at *e* and *f*. The orifice *e* is pref-

slag remains in contact with the coke in chamber *a* until its last traces of iron are removed and it has taken up the ash of the coke, when it is run off through a tapping hole *n*. The carbonic oxide may be utilized for heating the chamber *g*. It is burned at its formation above the bath by highly heated air in regeneration chambers *i*, set out with checkerwork of bricks, and communicating with chamber *g* by passages *f*. Each chamber communicates with chimney *o* by a passage *k*, the two conduits *k*, *k*, terminating at a door which conducts the waste gases of one regenerator to the chimney, while it allows the entrance of cold air to the other by orifice *a*. In this manner a high temperature is produced in chamber *g*, which facilitates the fusion of the ore and aids in its partial attack by the carbonic oxide gas, which traverses it in rising from the bath through the mass. This method of attacking the ore by the carbon dissolved in the bath, without mixing the solid carbon with the ore, in combination with the electric furnace comprising tubes and several chambers, and the process of heating a single chamber by the combustion of the carbonic oxide by means of air heated in Siemens regenerators is quite novel. It is stated that the electrical energy employed is utilized principally in order to compensate the losses of heat, and that it may be greatly reduced by careful construction of the envelopes of the furnaces in such a manner as to retain the heat as much as possible. The process is very interesting as showing the continuous development of the electrometallurgy of iron and steel, which is bound to show its possibilities when fostered by the progressive management of such large and well-known works as the Creusot.

**Glass-Melting Furnace.**—G. H. Benjamin, New York. Patent 762,270, June 14, 1904. Application filed January 3, 1903.

The furnace is illustrated in Fig. 2 in vertical section. It consists essentially of three chambers, 10, 11 and 12, of which the first one serves as preliminary heating chamber, the second comprises the electric furnace part proper, and the third constitutes the refining chamber. The charge is introduced through door 42, and slides down on the inclined hearth 14 of the heating chamber. The crown 16 of the latter is located at such a distance above the hearth as to permit a free radiation of flame within the fusion chamber, without touching the material upon the hearth 14. The heating of the chamber is accomplished by means of the hydrocarbon burners 19. The electric chamber 11 connects with the bottom of the heating chamber, and is wider at its bottom than at its top. It is divided into four inclined passages, which are not visible in the figure. Three sets of electrodes 21, 21, of carbon or other suitable material are provided in each passage, which melt the preheated material. After passing the arcs, the molten glass passes into the refining chamber 12, the rear portion 22 of which is wider than the front portion 23. The chamber 12 is between 32 and 48 inches deep, depending upon the character of the glass it is desired to make. On the bottom 25 of the chamber, a layer of chilled glass 24 is allowed to accumulate in order to prevent injury to the bottom blocks and their working up into the melted glass. The refining chamber is heated by hydrocarbon burners 27. The material is here subjected to a lower temperature, so that, when it reaches the front end of the chamber, it is in a condition to be gathered by hand through the gathering doors 40 or drawn into the receptacle 31, through passage 33. The material in receptacle 31 may be maintained at the required temperature in the chamber 13 by means of the hydrocarbon burners 28 until it is required for use. A plug 35 closes the opening 36, to prevent the flow of glass along the passage 33. A flue for carrying off the waste gases leads from the top of chamber 13 into the refining chamber 11 and a flue 39 leads from the latter around the electric chamber 11 into chamber 10. This construction, it is claimed, prevents the free carbon, which is stated to be contained occasionally in the products of combustion from the heating and refining chamber, from coming into contact with

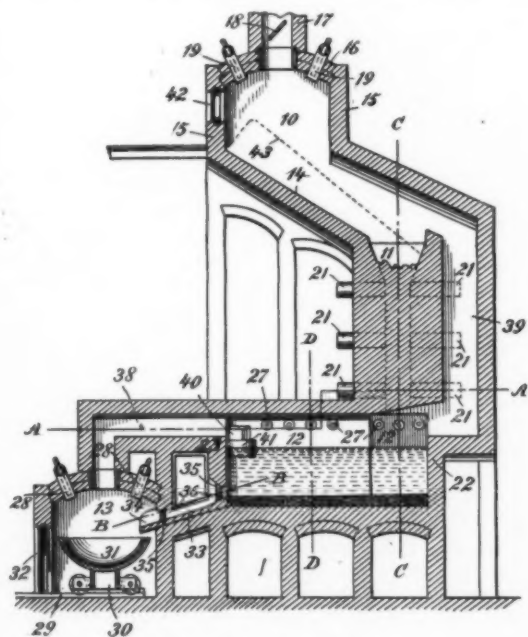


FIG. 2.—GLASS FURNACE.

erably slightly above the orifice *f*, so as to cause the metal to circulate from *a* towards *g* through passage *s*. The heating tube is provided with the magnetic heating cores *bb*. Coke or coal of any suitable kind is placed upon the bath of pig metal in the chamber *a*. Owing to the active circulation of the metal due to the heating of the tube 1, 2, the carbon, which dissolves in the molten bath, spreads to the chamber *g*. Ore and the necessary fluxes are introduced into chamber *g* in a uniform manner, which ore fuses in contact with the bath and is reduced by the carbon of the bath. The iron thus produced dissolves in the bath, while the carbonic oxide gas is liberated. The slag which results from the fusion of the gangue and still contains ore, is conducted into chamber *a* through passage *s*. The

and coloring the glass materials, while they are in the zone of the highest temperature.

#### ELECTROLYTIC PRODUCTION OF METALS AND COMPOUNDS.

*Process of Recovering Metals from Ores or Sands.*—W. J. Jory and J. H. Jory, San Francisco, Cal. Patent 760,539, May 24, 1904. Application filed April 7, 1903.

The electrolytic part of the proposed process is carried out in the apparatus patented by the same inventors and described in *ELECTROCHEMICAL INDUSTRY*, Vol. II., p. 238. Among the various processes outlined are the following. Gold ores containing copper and iron sulphides are treated by introducing a solution of sulphuric acid or other single acid in the pulverizing apparatus, the acid acting upon ferric sulphide to produce a solution of ferric sulphate, to act as solvent for both the copper and the gold contents of the ore. When the latter contains gold, arsenic and antimony in connection with sulphur combined with this or other metals, the procedure consists in adding ammonium sulphide to the ore in the pulverizing apparatus, it being stated that the reaction which takes place between the arsenic or antimony and the reagent forms a solution which dissolves the gold and keeps it in solution. In treating a silver ore containing copper and silver sulphide, in some cases a sulphate of some alkaline earth or alkali metal is used, "preferably sodium hyposulphite," to which, during the process of pulverization, a solution of ammonia in such quantity as will produce a decided alkaline reaction, is added. Precise information as to the various processes is lacking. It is also proposed to recover mercury from ores by electrolysis instead of distillation, by pulverizing the ore in contact with preferably an alkaline sulphide with an addition of an alkali hydrate to obtain an alkaline reaction of the solution. The ore pulp, together with the solvent, is then run into tanks provided with filtering beds and remains until the mercury goes in solution. The solution is then filtered off and the mercury deposited in the apparatus described on page 238, as mentioned above. Data as to voltage, current density, strength of solutions, etc., are not given.

*Reduction of Nitro Compounds.*—Max Buchner, Mannheim, Germany, assignor to C. F. Boehringer & Soehne. Patent 761,284, May 31, 1904. Original application filed September 24, 1900. Divided and refiled December 13, 1902.

The invention consists in the reduction of nitro compounds to amines by passing the electric current through such compounds in acid solution in the presence of lead or a lead salt. The electrolysis is carried out in a vessel divided into two compartments by a porous diaphragm. It is unimportant what material is used for the cathode, as the latter merely serves to convey the current, the process of reduction being solely dependent upon the presence of the above metal in the cathode chamber. It is also immaterial whether the finely divided metal or metallic salt is added to the electrolyte in the cathode chamber. In both cases the reaction proceeds over or by way of the regenerated or recovered metal. The process of the reduction of nitrobenzene to aniline, by the addition of lead chloride to the cathode electrolyte, is carried out as follows. The electrolyte of the anode chamber consists of a 10 per cent solution of sulphuric acid; the anode is any suitable indifferent conductor. The cathode contains a mixture of five hundred parts, by weight, of fuming hydrochloric acid, five hundred parts, by weight, of water, 123 parts, by weight, of nitrobenzene, and fifty parts, by weight, of lead chloride. The cathode is a cylinder of platinum. The nitrobenzene is constantly stirred by a rapidly revolving stirrer, and is constantly replenished when consumed. A cooling device, such as a cooling coil, is preferably used in the cathode compartment. The current density is about 1900 amperes per square millimeter (evidently a misprint). The current is maintained until regular liberation of hydrogen takes place and becomes visible. After the process of electrolysis is completed, the lead of the lead chloride is found to have separated in the

form of fine metallic sponge, and no lead is found in the cathode electrolyte. The reduction of nitrobenzene to aniline by the addition of metallic lead to the cathode electrolyte is carried out in substantially the same manner, except that instead of the lead chloride forty parts of finely divided metallic lead are added to the cathode electrolyte.

*Preparation of Azo Dyes.*—Walter Loeb, Bonn, Germany, Assignor to C. F. Boehringer & Soehne. Patent 761,310, May 31, 1904. Application filed March 16, 1903.

Azo bodies have hitherto been prepared by dissolving or suspending an Amine in acid solution, diazotizing it at a low temperature by means of a nitrite and mixing it with the solution of a coupling compound. Coupling is the property which certain bodies (among them the amines and phenols) possess of combining with diazo compounds to form azo compounds. Coupling compounds are the compounds which take part in such combination, *e. g.*, amines or phenols on the one hand and diazo bodies on the other. Dr. Loeb has succeeded in preparing azo dyes electrochemically in one process by combining diazotation and coupling of the amine with a compound of acid character in the same solution under the influence of the electric current. The principle of the operation is stated to depend on the discharge of  $\text{NO}_2$  anions in a nitrite bath at the anode. When an amine is present, its diazotation takes place. Such diazo compounds are, however, very unstable, but by employing coupling compounds in connection with the diazoting reaction, a stable azo dye can be obtained. If a coupling compound of an acid character is present during diazotation, it will at once combine with the diazo compound, which is formed and produce the corresponding azo compound or dye. The amines cannot be used for the process of coupling, on account of their being subject to diazotation by the  $\text{NO}_2$  ions. The process is explained by assuming that the reaction of coupling takes place at a much greater rate than the decomposition of the diazo bodies. The process is preferably carried out in a vessel separated into two compartments by a porous diaphragm. A platinum anode is preferable; the cathode may be of any metal. An amine, the coupling compound, preferably in the form of a soluble salt, and nitrite, preferably in the required molecular proportions, are introduced into the anode compartment, all in aqueous solution or suspension. The reaction is expressed by the following general equation:  $\text{RNH}_2 + \text{H.R'.OH} + \text{HNO}_2 = \text{R.N:N.R'.OH} + 2\text{H}_2\text{O}$ . The preparation of the sodium salt of aniline-azo-2-naphthol-3,6-disulphonic acid (Ponceau 2 G.) is carried out by preparing an anode bath of 10 parts, by weight, of aniline, 32.7 parts, by weight, of "R acid" (B naphthol disulphonic acid) and 9.1 parts, by weight, of potassium nitrite, stirred with 100 parts of water, and a cathode bath of a dilute potassium hydrate solution. The anode is platinum and the cathode nickel. The current density may be varied from 0.5 to 7.5 amperes per square decimeter, the temperature from 40° to 90° C. After rather more current than is necessary to decompose the nitrite has passed, electrolysis is stopped and the dye isolated from the deep red anode solution as usual. From an anode solution of 10 parts benzidin, 33 parts naphthionic acid, 9.3 parts potassium nitrite and 100 parts water at 60° to 90° C. there results the dyestuff Congo. From 10 parts diamisidine, 13.6 parts sodium salt of B naphthol, 7 parts potassium nitrite and 100 parts water at 60° to 90° C. results a deep violet dye. From 8 parts naphthylamine sulph. acid (1.4), 10.7 parts R acid, 3 parts  $\text{KNO}_2$  and 100 parts water, a deep red solution results, from which the dye may be separated by direct evaporation or the addition of salt. From 11 parts sodium salt of toluylene diamine sulph. acid, 11 parts R acid, 6.2 parts  $\text{KNO}_2$  and 100 parts water at 15° to 30° C. the dye may be obtained as in the preceding case. The dye tropaeolin 000 No. 1 is obtained from 11 parts sodium salt of sulphanilic acid, 8.5 parts of a naphthol sodium salt, 4.4 parts of  $\text{KNO}_2$  and 100 parts water at 15° to 30° C. The dye Rocelline is gotten by using 10 parts sodium salt of 1.4

naphthylamine sulphonic acid, 6.8 parts sodium salt of B naphthol, 3.6 parts  $\text{KNO}_3$  and 100 parts water at  $15^\circ$  to  $30^\circ$  C. The dye Hessian brown is obtained from 9.2 parts benzidine, 31.6 parts azo compound prepared from sulphanilic acid and resorcin, 6.9 parts sodium nitrite and 100 parts of water at  $20^\circ$  to  $90^\circ$  C.

**Anode and Process of Making Same.**—Henry Blackman, New York. Patent 762,227, June 7, 1904. Original application filed December 8, 1896. Divided and refiled April 24, 1903.

The invention relates to the preparation of anodes for electrolytic purposes, especially the electrolysis of sodium chloride. A plate of cast iron, preferably, is oxidized on its surface, so as to convert it into magnetic or electroconductive oxide, until the coating is of sufficient thickness. That part of the plate where it comes into contact with the surface of the electrolyte, is protected by a band of insulating and impervious material, such as glass or a vitreous glaze. The oxidation of the plates is suitably effected by heating them in a retort to form  $1000^\circ$  to  $1200^\circ$  F., and then passing superheated steam over them for eight or ten hours, or until the coating attains a thickness of from one to three millimeters.

A small quantity of naphtha or other light hydrocarbon is advantageously injected into the retort during this process. The oxidation may also be effected by first coating the iron plate with a thin film of some other metal, as tin or bronze, and then exposing it to a current of oxidizing gas, while heated to about  $1000^\circ$  F. or upwards, whereby the film of coating material is stated to disappear. The oxidation may also be brought about by dipping the plates into a bath of fused niter containing a small percentage of peroxide of manganese, which is kept at about  $650^\circ$  F. in an ordinary melting pot, and leaving them until the surfaces are oxidized to the required depth.

#### STORAGE BATTERIES.

**Storage Battery Plate.**—E. W. Smith, Philadelphia, Assignor to Electric Storage Battery Co. Patent 760,712, May 24, 1904. Application filed September 10, 1903.

The invention relates to that type of storage battery plate, which comprises a grid, the faces of the respective openings of which are covered by a perforated shield and means are disclosed for securing the perforated cover plate to the grid. Claim No. 1 reads: Means for connecting the grid and perforated cover plate, which comprise grooves in the cover plate, and projections cast from the grid and engaging perforations of the plate and occupying the grooves thereof.

**Storage Battery Plate.**—Achille Meygret, Paris, France. Patent 760,897, May 24, 1904. Application filed June 29, 1903.

The plate is shown in side elevation in Fig. 3, without the active material. It is preferably made of sheet metal cast, stamped, or otherwise shaped into form. It has an end piece *a* to furnish supports for the strips *b*. Each strip has a series of perforations *c* for holding the active material, which is spread on both sides of the plate. A rib *b* extends around the border of the plate and of each strip *b* for the purpose of stiffening. In order to prevent the loosening of the active material, an elastic sheath, unattackable by the electrolyte, is formed over the surface of the plate by dipping the latter into a bath consisting of castor oil, essence of turpentine, octonitric

cellulose and ordinary nitrate of cellulose of commerce, the tetranitrate of cellulose being preferred. In order to allow the electrolyte to reach the active material, this sheath should be rendered porous by chemical or mechanical means.

**Storage Battery.**—Th. A. Willard, Cleveland. Patent 761,345, May 31, 1904. Application filed September 11, 1903.

The invention concerns a sheath or envelop for separating and containing the storage battery plates. It consists of an envelop of hard rubber, made in two parts, perforated and ribbed, which are joined together with a strip of soft rubber, extending all around the meeting edges of the two parts. After being applied, the strip is vulcanized.

**Storage Battery Electrode.**—J. von der Poppenburg, Charlottenburg, Germany. Reissue 12,228, June 7, 1904. Original 701,389, June 3, 1902. Application for reissue filed November 12, 1903.

The plate is so constructed that the cross-pieces adapted for dividing or separating the active material protrude from the frame on both sides. They are provided with holes through which pass elastic bars which press against protecting strips which prevent the active material from dropping off. Frames, cross-pieces and bars are made of ebonite.

**Electrical Accumulator.**—Q. J. B. M. Colletas, Paris, France.

Patent 762,803, June 14, 1904. Application filed September 12, 1901. Renewed April 22, 1904.

The battery is composed of a cell made of insulating material, which contains an aqueous solution of sulphate of copper at its highest degree of conductivity, (17 per cent), strongly acidulated with sulphuric acid. The cathode is made of agglomerated retort carbon, preferably associated with metallic arsenic. The body of the anode is also of agglomerated carbon, preferably of double T-shape. A layer of plumbiferous paste is introduced into the space formed by the web and the sides of the double T. The plumbiferous paste is obtained by mixing either red lead or protoxide of lead or chloride of lead with water containing one-twentieth of liquid gelatine, white of eggs, dextrine, liquid starch or vegetable gums, to a firm and plastic consistence. These materials being converted into soluble products upon electrolysis and leaving the remaining active mass in a porous condition. A wire of lead is wound around the paste to keep it in place. The reactions during charge and discharge are claimed to be as follows. A current is passed of at least 2.5 volts, and exceeding one ampere per square decimeter of cathode surface. Under the action of this current the hydrogen is carried to the cathode and takes with it the copper, which is deposited on the cathode in the form of copper hydride ( $\text{Cu}_2\text{H}_2$ ), whereas the oxygen at the anode converts the lead into peroxide. Upon discharge the sulphuric acid attacks the copper hydride, forming sulphate of copper and liberating the hydrogen, while at the anode the peroxide of lead is reduced to the oxide. Further data are wanting.

**Storage Battery.**—Max Schneider, Dresden-Plauen, Germany.

Patent 762,847, June 14, 1904. Application filed September 4, 1903.

The battery as illustrated in the specification, shows an outside containing vessel and cover of insulating material, between which vessel and the negative pole electrode is introduced a fibrous cellulose sheet chemically treated with a neutral salt, for insulating purposes. The cylindrical cathode is made of metal or active material as usual, and slit vertically, and a central vertical partition wall extends into the slit. Another insulating sheet as above separates this cathode from the anode, which is built up of a number of downwardly converging lead cones, provided with radial and cross-ribs for retaining active material. These cones are put one above the other and fastened to a tubular core by melting. The whole is then cut in halves, the two parts melted to a fork, and the structure so introduced into the vessel that the fork rests on the above-mentioned partition wall.

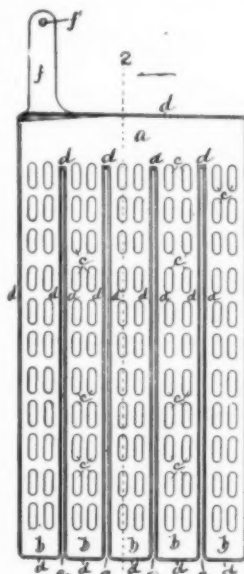


FIG. 3.—STORAGE BATTERY PLATE.



## GALVANIC ELEMENTS.

*Process of Manufacturing Hard Porous Electrodes for Batteries.*—H. P. Poerske and G. A. Wedekind, Hamburg, Germany. Patent 760,561, May 24, 1904. Application filed November 18, 1903.

The process consists in hardening pure metallic oxides or pure metallic powders, to which no foreign additions, however, have been made, by means of chlorine compounds of whatever metal is used. For instance, oxide of copper is stirred to a fairly consistent paste in a solution of protochloride of copper and fine copper filings are stirred in. This paste is put into molds and heated for about half an hour to 100° C. Then the plate is electrolyzed with the object of setting free the oxygen and chlorine. It is claimed that such an electrode does not dissolve in alkaline solutions.

*Exciting Fluid for Electrical Batteries.*—G. F. Atwood, Wakefield, Mass. Patents 761,641 and 761,649, June 7, 1904. Applications filed October 3, 1903.

The inventor claims in the first patent a composition for use in the cell of electrical batteries, in which the negative or zinc element is immersed, consisting of ammonium carbonate 1½ pounds, carbonate of sodium 10 ounces, bisulphate of mercury 10 ounces, and sufficient sulphuric acid to make the specific gravity of 30 gallons of water 1.2. The second patent covers a composition for use in the cell of electrical batteries, in which the positive element is immersed, consisting of nitrate of sodium 7 pounds, nitric acid 142 pounds and sufficient sulphuric acid to make the spec. gr. of fourteen gallons of water 1.2.

*Electrical Battery.*—J. R. Lord, San Francisco. Patent 762,425, June 14, 1904. Application filed June 5, 1903.

The principle of this battery is the employment of a compound of the anode metal as the active anode material and the replenishing of the latter in such a manner that it is constantly precipitated upon the anode from the electrolyte. The illustrations show a form of cell, presumably rectangular, with the anode on the bottom and above it, in a horizontal position, the cathode. The general claim is for an electric battery having an anode composed of an electrical conductor upon or around which is placed or deposited a quantity of a compound of an anode metal, such conductor serving as negative pole and being placed in such a position that any solids chemically precipitated from the electrolyte may fall in proximity thereto, such solids thereby forming anode active material; having an electrolyte composed of one or more salts of one or more anode metals in solution; and having a cathode composed of any conducting substance chemically unattacked by the electrolyte.

*Electric Battery.*—J. E. Haschke, Chicago. Patent 762,715, June 14, 1904. Application filed February 8, 1904.

The construction of the battery shows a metallic receptacle which contains a series of cells. The latter are made up of unipolar negative-pole plates, which constitute the outside-end plates of the first and the last cells of the series, bipolar active plates, which separate the cells from each other, and a

number of supplemental plates of alternating polarity in each cell. Provision is made to get the individual cells liquid tight, and the series is held together by tie-rods and nuts. The supplemental plates are preferably shorter than the cells and perforated, in order to allow the free circulation of the electrolyte. The principle can be applied to primary or reversible cells.

## MISCELLANEOUS.

*Method of Purifying Water.*—V. M. George, Youngstown, O. —Patent 761,044, May 24, 1904. Application filed January 8, 1904.

The method consists in passing the water through an apparatus where it is subjected to electrolysis, thence through a filtering vessel filled with a layer of tripoli as filtering material and finally through an ozonizing tank. The apparatus for electrolyzing comprises a tank, in which are arranged four plates nearly square or rectangular. The lowest is made of copper, the next of an aluminium-nickel alloy, the third of zinc and the fourth of carbon. The plates of carbon and of aluminium-nickel are connected to one pole, the zinc and copper plates to the other of the source of current.

*Clarifying and Filtering Apparatus.*—D. L. Watson, New Orleans. Patent 761,187, May 31, 1904. Application filed October 2, 1903.

The apparatus comprises four cylindrical tanks disposed within a larger tank. The first one of these tanks contains an electrolyzer, disposed on both sides of a partition, which reaches nearly to the bottom of the tank and forces the water to travel downward on one side of the tank and upwards on the other side. It is thus twice subjected to the influence of the current. From the first tank it passes into the second, where it encounters a filtering body of charcoal, sand and quartz, after passing which it is led into the third tank, where it has to pass another filtering body of stone. It is then discharged into the large containing tank, ready for use. The fourth tank serves for the introduction of ice or any other suitable cooling agent. The electrolyzers are constructed of a horizontal frame of marble, provided with grooves, in which plates of platinum or other suitable material are seated. Alternate plates are connected with the positive and the negative poles of a source of current.

*Explosive Cartridge.*—Giovanni Cornara, Mantova, Italy. Patent 762,229, June 7, 1904. Application filed December 31, 1897.

The cartridge is formed of an outside reservoir, strong enough to stand the pressure exerted by the gases generated within, which serves at the same time as cathode. The electrolyte is a 5 per cent solution of caustic potash or soda. An anode is introduced insulated into the reservoir and the solution is electrolyzed with a current not exceeding 7 amperes per square decimeter of anode surface. The gases resulting from the electrolysis are exploded by means of a cap, a fuse, or a metallic wire rendered incandescent by the passage of an electric current.

## SYNOPSIS OF ARTICLES IN OTHER JOURNALS

*A Summary of Articles on Electrochemistry and Allied Subjects Appearing in American and Foreign Periodicals.*

## INDUSTRIAL ELECTROCHEMISTRY.

*Cyanide Process.*—The *Engineering and Mining Journal* of May 3, contains an article by C. M. FASSETT on the Hendryx electrocyanide process, for which the following claims are made; that it is applicable to any ore, the values of which are soluble in cyanide solution or which can be made so by preliminary treatment; that extraction and deposition of the gold

and silver are carried on simultaneously; that the extraction can be made in much less time and with less amount of chemicals than by the old processes, on account of perfect agitation, the aeration and regeneration of cyanide by the electric current. No special qualifications are said to be required in the crushing machinery. "The more slime the better." The process is stated to be adapted to handling tailings and slimes from metal-

lurgical plants already equipped and running. The first cost of installation and the cost of operation are stated to be small. The process is described as follows:

The ore is crushed (preferably in a dilute cyanide solution) and run into the agitator, together with enough alkali to overcome the acidity of the ore, and enough cyanide to bring the strength of the solution up to about 1 pound per ton. The bulk of the solution used is from one to two times the weight of the dry ore. The charge is then agitated, and as the precious metals are dissolved, they are deposited on the plates in metallic form, by the agency of an electric current of low intensity furnished by a small dynamo. As soon as the assays show that the extraction is complete, a valve is opened in the bottom of the agitator, and the charge runs into a settling tank, whence the settled pulp is sluiced to waste and the clear solution

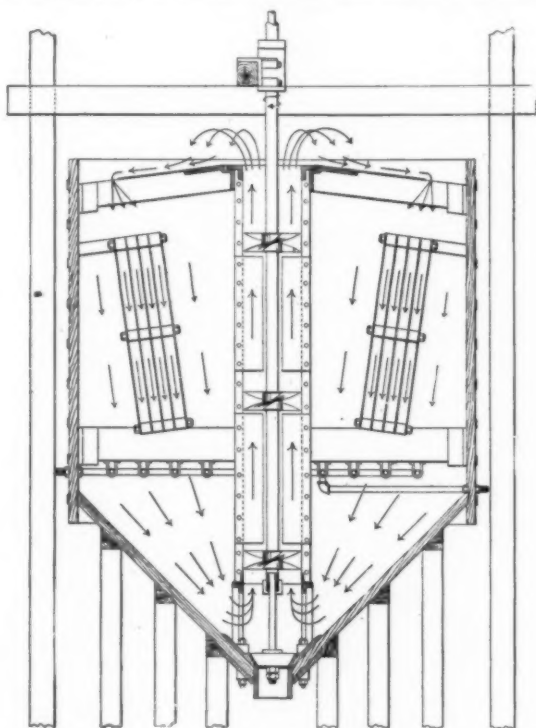


FIG. 1. AGITATOR FOR CYANIDE PROCESS

pumped back to storage. The essential mechanical feature is the agitator illustrated in Fig. 1. It consists of a cylindrical tank having a conical bottom of 45° pitch. In the center of the tank is a circular well, which extends nearly to the top and bottom, supported by braces from the sides of the tank, and having a circular apron at the top which slopes gradually toward the circumference. In this well is a hollow shaft, carrying a driving pulley at the top and three screw propellers in the well. The discharge valve is connected to a valve stem which passes through the hollow shaft and is operated by a hand wheel located above the driving pulley. Outside the well, and between the apron and the bottom of the tank, the anode and cathode plates are supported from the sides of the tank and supplied with the electric current. A coil of pipe serves for raising the temperature of the charge by means of steam or hot water passed through it. The revolution of the propellers in the well produces a strong upward current there and results in a rapid and uniform circulation of the whole charge upward through the well and downward among the electrically charged plates, as indicated by the arrows in the drawing. It appears that an experimental plant in the author's laboratory has been working for six months successfully, but that the process has not yet been applied on a large scale.

**Electro-Magnetic Concentration of Iron Ore.**—The utilization of low-grade magnetic iron ores is practically dependent on magnetic concentration. In the United States this concentration is practised on a large scale, followed frequently by briquetting, using lime as a binder. The Gröndal process, as used at Herräng, Sweden, consists in briquetting by pressure alone, then roasting to a hard brick. The ores at Herräng, according to a paper of H. LOUIS, before the *Iron and Steel Institute*, carry 1 to 1.5 per cent sulphur, and when the briquetted concentrates are roasted at about 1300° C. the sulphur is expelled, and the ore converted largely into ferric oxide and agglutinated into very strong briquettes. This roasting is done in a tube 145 feet long, the briquettes taking twenty-four hours to pass through; the fuel used is blast-furnace gas, and the power for the crushers and separators is also obtained from the same source, using gas-engines. The blast-furnace thus furnishes the means of preparing the ore, when its gases are properly utilized.

A fully illustrated article by C. Q. PAYNE in the *Engineering and Mining Journal* of June 23, gives an account of the magnetic concentration of zinc ore in various mines of Virginia. The schemes of the treatment in use at the Withe mine, and at the Delton mill of the Clark mine, are described and illustrated by diagrams. At the latter mill four magnetic separators are arranged, tandem in pairs, the first pair producing a rough zinc concentrate and clean iron tailings, while the second pair, which retreats the rough zinc concentrate, produces therefrom a clean concentrate and a certain amount of middlings, which are repassed over the first set of machines. These separators were designed by the author and the design is based on the fact that in the separation of feebly magnetic minerals, such as limonite, garnet, etc., a very powerful or dense magnetic field is not so important as one in which the position of the lines of force are so controlled that great differences of magnetic density are established therein. The design of the separators is described and illustrated.

**Explosions Produced by Ferro-Silicon.**—Additional information concerning the explosions of casks containing ferro-silicon, at Liverpool, was given by A. DUPRE in a communication to the *Iron and Steel Institute*, on May 5 last. The material causing the explosions contained silicon 59.40 per cent, iron 36.85, manganese 0.08, aluminium 2.73, calcium 0.14, magnesium 0.17, carbon 0.218, sulphur trace, phosphorus 0.056 per cent. The gas from a cask was analysed and showed hydrogen phosphide and hydrogen arsenide, and it is to the former that M. Dupre ascribes the explosions, stating that experiment has shown that 4 kilograms of powdered ferro-silicon would make 64 liters of air explosive. The precautions suggested were to fill up the drums with paraffin oil of high flash point, or to ship only solid ingots, well tarred and tightly packed. In the discussion, Mr. Watson Gray stated that 25 per cent and 75 per cent ferro-silicon did not disintegrate, but that the 50 per cent quality did, even if dipped in paraffin wax to keep out moisture. Calcium was not the cause of this, since 40 per cent ferro-calcium is quite permanent, even in damp air. Mr. J. E. Stead attributed the disintegration to calcium phosphide, which is soluble in melted ferro-silicon and is excluded as an envelope around each crystal as the mass sets. Professor Le Chatelier thought that the calcium silicide present produced hydrogen silicide, which was spontaneously inflammable. The paper and discussion are highly interesting to electrometallurgists.

**Electrolytic Preparation of Chloroform from Acetone.**—The May issue of the *Journal of the American Chemical Society* contains a paper by J. E. TEEPLE, showing that his recent method for electrolytically preparing iodoform may also be applied to the production of chloroform. From his former work the following scheme suggested itself; electrolysis of a chloride solution in the presence of acetone under conditions which would continuously give the greatest possible yield of hypochlorite, i. e., at a temperature below 25° C., with a solution

containing no alkali or as little as possible, with a high current density at the cathode, and a comparatively low one at the anode. The following arrangement of the experiments may be used. In an ordinary cylinder of 150 to 200 cc capacity, 100 cc. of water are placed, with 20 grams NaCl and 4 cc. acetone. A platinum cylinder serves as anode and a platinum wire as cathode. The vessel is closed with a cock connected with a reflux condenser and the apparatus is cooled with running water. During electrolysis a slow stream of chlorine is passed, as needed to neutralize the alkali. The anode current density is about 6 amperes per square decimeter or less. After 8 to 10 ampere-hours a small layer of chloroform may be removed from the bottom of the electrolyte by a pipette and more may be obtained by distilling the solution with steam. The amount of chloroform thus obtained, does not represent the whole current action in that direction, nor is it the whole of the chloroform actually formed, for a considerable part is still held in solution by the acetone; but if the process were run continuously on an industrial scale, there would be no loss from either of these sources.

**Electrolytic Preparation of Bromoform.**—In an article published in *Zeit f Elektrochemie*, June 17, E. MUELLER and R. LOEBE describe a similar method for preparing bromoform by electrolysis of solution of potassium bromide in presence of acetone. Coughlin had developed such a method in which he used a diaphragm cell. He used in the anodic compartment a solution of 25 grams KBr 10 cc. acetone and 75 cc. water. During electrolysis, which was carried out at about 25° C, with an anodic current density of 0.04 ampere per square centimeter, gradually 3 grams of sodium carbonate were added. The cathodic compartment contained a solution of 10 grams of sodium carbonate in 100 cc. water. The present authors have found that it is not necessary to use a diaphragm, if special means are applied to prevent reduction at the cathode. For this purpose chromate is added to the electrolyte; the addition of chromate has been applied by Mueller for similar purposes before. During electrolysis a current of carbonic acid is passed through the electrolyte. Good results were obtained, for instance, with the following arrangement. A glass beaker was filled with 140 cc. of a 25-per-cent solution of potassium bromide to which was added 0.02 per cent potassium chromate; also 20 cc. of acetone and 20 grams of solid potassium chromate. A platinum sheet of 30 square centimeters surface was used as anode, and a spiral platinum wire as cathode. The current was 2 amperes and carbonic acid was passed through the solution. The temperature was 15° C. At the end of the experiment 20.58 grams of bromoform had been obtained, corresponding to an ampere-hour efficiency of 90.2 per cent.

**Diaphragm Cells for Electrolysis of Sodium Chloride.**—The *Journal de Chimie Physique* of March, April and May contains a long paper by A. TARDY and P. A. GUYE on diaphragm cells for the electrolytic production of caustic soda and bleaching powder. The experimenters used a greater number of diaphragms of different make, and found that in order to define the action of a diaphragm it is necessary to make two measurements; the first is a measurement of the porosity and the dimensions of the diaphragm, the second a measurement of its (mechanical) permeability. These two measurements may be supplemented advantageously by a diffusion experiment. The first two experiments are made with water, the third one with an electrolyte with a known co-efficient of diffusion. By means of these measurements it is possible to give at once those quantities which represent characteristic features of the nature of the diaphragm. The authors distinguish five characteristic features of a diaphragm and show how, on the basis of the above measurements, numerical values can be derived for these characteristic features. A longer abstract of the paper will be given in our next issue in a separate article.

**Fixation of Atmospheric Nitrogen.**—This subject, which has

aroused special interest on account of the experimental trial on a large scale by the Atmospheric Products Company at Niagara Falls, has also attracted other inventors. Some references are herewith given to recent papers. An investigation by MUTHMANN and HOFER is found in *Ber. D. Chem. Ges.*, 1903, 2, 438, and an investigation by RASCH in DINGLER'S *Polyt. J.*, 1903, 17, and a paper by C. BRANDT in *Rev. Gen. Ch. Pure. et Appl.*, 1903, page 517. The latter author proposes to use electrostatic machines, furnishing directly oscillatory discharges at high potentials. A paper by VON LEPEL is published in *Ber. D. Chem. Ges.*, vol. 37, page 712, March 12, 1904. He discusses the relation between arc, temperature and output of nitric oxide by electric discharges through air. He made experiments with a rotating anode. The output is increased by impregnation of the cathode with certain salts. For instance, other things being equal, i. e., with equal speed of rotation, and at the same temperature, he obtained 64 mg HNO<sub>2</sub> if the cathode was wetted with water, against 126 mg if it was wetted with KOH.

**Copper.—Metallurgie** of June 8 contains a long illustrated article on copper mining and treatment on the works of the Mansfeld district in Germany. These mines have been worked since the year 1200, but the greatest extensions were made during the last 50 years. The output of copper was 18,749 tons in 1902 (against 1,485 in 1861), that of silver 98,445 kg. (against 8,008) and the number of workmen 19,883 (against 4,677). The article contains a great amount of statistical information on the development of the works. In connection with the works there is an electrolytic refinery which is supplied with power partly from two gas-driven generating sets, each of 120 hp., utilizing blast furnace gases.

#### THEORETICAL AND EXPERIMENTAL.

**Silver Voltameter.**—With the ordinary type of silver voltameter the results so far obtained have been not quite satisfactory. T. W. Richards has pointed out that the main trouble arises from the formation of a complex ion at the anode which, when transported to the cathode, will deposit too much silver. To prevent the anode liquid from reaching the cathode, he surrounds the anode, which is a silver rod, by a porous fine-grained cup, and keeps the level of the electrolyte in this cup always lower than that of the outside. Leduc, on the other hand, hopes to prevent the formation of the disturbing ion by using a very small current density at the anode; he therefore employs as anode a mass of the granulated silver surrounded by filter paper. In an American Physical Society paper which is abstracted in the June issue of the *Physical Review*, K. E. GUTHE describes a series of experiments which were made to compare the different forms of the silver voltameter in a severe test. He finds that the usual type of silver voltameter is not a very reliable instrument for measuring quantity of electricity. Leduc's type does not prevent the formation of the complex ion even with a small anode current density; the use of filter paper should be avoided. Silver in contact with the anode liquid breaks up the complex ion. Richards' type is the only satisfactory form so far proposed, and gives very consistent results. For convenience in manipulation, Guthe has modified it in such a way as to avoid the necessity of removing, by frequent pipetting, the anode liquid from the bottom of the porous cups. Finely divided silver is placed at the bottom of the cup and this effectively removes the complex ion. In order to insure a constant resistance of the voltameter it was found necessary to surround the lower part of the porous cup by a small glass beaker. A second type proposed by Guthe is the large silver anode voltameter; granulated silver is placed in a layer about 0.5 cm. deep at the bottom of a large porous cup; upon this is pressed the silver plate forming the anode connection. The whole is immersed into the platinum bowl (the cathode), containing a neutral 20 per cent solution of silver nitrate. In an extended series of tests in which currents ranging from 0.2 to 1.5 amperes



were employed, the results obtained with the Richards type, and with the two types designed by the author, were very consistent, the largest variation of any single value from the mean not exceeding one in 20,000, except when a current of only 0.2 ampere was used.

**Mobility of Ions in Liquid Ammonia Solutions.**—The May issue of the *Journal of the American Chemical Society* contains a paper by E. C. FRANKLIN and H. P. CADY, giving the results of an extended investigation of ionic mobilities in liquid ammonia solutions. The authors have developed an apparatus which is essentially an improvement and modification of the method of Lodge and Masson for determining the mobility of ions directly by observing the movement of a colored boundary surface. They determine the velocities of a number of univalent ions in liquid ammonia at  $-33^{\circ}$  C. These were found to be 2.4 to 2.8 times as great as they are in aqueous solutions at  $18^{\circ}$  and the values were found to be in agreement with the velocities calculated from conductivity measurements by the method of Kohlrausch.

**Copper Analysis.**—A rapid and convenient method for the quantitative electrolytic precipitation of copper is described by T. W. RICHARDS and H. BISBEE in the May issue of the *Journal of the American Chemical Society*. The consideration of the conditions necessary for a quick quantitative electrolytic precipitation shows that among the essential ones are the concentration of the solution and the area of the electrode. In the method described by the authors, these conditions are made as favorable as possible by concentrating the electrolyte and placing it between two large surfaces in a thin film, such as the annular space between two crucibles separated by a tripod like device of thin glass rods. As the concentration of the electrolyte diminishes during electrolysis, the current strength is diminished, either in steps by the operator or automatically by employing a single storage cell with resistance. The time required for complete precipitation is inversely proportional to the concentration of the solution if the cathode surface is unchanged.

**Semipermeable Diaphragm.**—In an article published in *Zeit. f. Elektrochemie*, May 13, J. SEBOR deals with the speed of diffusion of water through a semipermeable diaphragm. The speed of diffusion is nearly directly proportional to the osmotic pressure of the dissolved substance, so that there might be a possibility to use such a method for determining osmotic pressure, etc. The speed of diffusion decreases with the temperature.

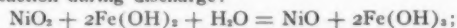
**Electrolytic Analysis.**—In two articles published in the *Zeit. f. Elektrochemie*, June 3, L. AMBERG discusses the use of revolving electrodes for decreasing the time required for electrolytic analysis and gives some notes on the electrolytic deposition of palladium.

#### BATTERIES.

**Edison Alkaline Battery.**—*Electrical World and Engineer* of May 7 contains a longer abstract of R. A. FLIESS' paper, which was noticed on page 169 of our May issue.

**Jungner Battery.**—A shorter communication by M. U. SCHOOP in *Elek. Zeit.*, May 26, and a longer article by the same author in *Centralblatt f. Accum.*, June 15, deal with the history of the Jungner accumulator and the question of priority between Edison and Jungner. In the former communication Schoop says it is unfair to use his experiments with an old Jungner nickel-cadmium cell (*ELECTROCHEMICAL INDUSTRY*, September, 1903, page 465) to make comparisons with the Edison battery, since his former article referred rather to the theory of the alkaline accumulator. "Dr. Jungner knew very well the weak points of his nickel-cadmium and nickel-iron cells which had been made with insufficient means and machines. For this reason he has not placed his cells on the market. On the other hand, Dr. Jungner is justified in claiming the priority of having invented the alkaline accumulator with constant electrolyte." In the article in the *Centralblatt* Schoop gives a long review of the history of the subject.

Jungner began to work along these lines in 1892; he started from the old copper-zinc combination in alkaline solution and tried oxide of copper as one electrode against many different metals as the other; to increase the conductivity of the active masses he added powdered graphite (English patent, October 23, 1895); in 1896 he embedded his active materials between perforated metallic plates (English patent of 1897). The data of Jungner's Swedish patent for the nickel-iron combination is January 29, 1901; he gives there the following formula for the reaction during discharge:



Schoop emphasizes that he and Jungner are convinced that if a comparison is made between the alkaline accumulator and the lead accumulator concerning the cost of manufacture on the basis of watt-hours per unit of weight, the cost of the nickel-iron cell is certainly not higher than that of the lead cell; the active iron material can be made by a very simple and cheap method and this fact counterbalances the higher cost of the nickel. Schoop's article is concluded as follows: "Between Jungner's invention and that of Faure there is a certain obvious analogy, in so far as Faure's patent 19,026, of February, 1881, which was of greatest and decisive importance for the manufacture of lead accumulators, protected to a certain extent the general principle of making lead accumulators of high capacity in a short time. In his patent specification C. A. Faure had given detailed instructions for the manufacture and formation of the active materials, and for the use of porous diaphragms. Nevertheless, it is well known that nobody has succeeded in making commercially satisfactory lead cells on the basis of nothing but Faure's instructions; this became possible only by the use of a grid as support of the active material; this had not been provided for by Faure. But the principle, on the basis of which lead cells with high capacity could be made in a short time, was given in Faure's patent, and every manufacturer who wanted to apply a quick formation—i. e., not according to Planté—was obliged to recognize Faure's patent."

(Mr. Schoop is the chief engineer of the German storage battery manufacturing concern, which has bought Dr. Jungner's German patents.)

#### MISCELLANEOUS.

**The Thermal Efficiency of the Blast Furnace** is a subject interesting to any one having to do with furnaces, be they fuel or electric in their nature, and Mr. W. J. FOSTER presented to the *Iron and Steel Institute* recently the results of the most thorough investigation which has been made in this direction since I. Lowthian Bell's classical researches. The data are too copious to be reproduced in abstract, but show practically 50 per cent of the calorific power of the fuel to be contained in the gases as combustible power, 15 per cent to be absorbed in reductions, and 15 per cent to exist as sensible heat in the pig iron, slag and gases. Electrometallurgists will find food for reflection in making comparison with the thermal efficiency of electric furnaces, such as calculated by Dr. J. W. Richards (this journal, October, 1902, page 46), and the comparison is to the advantage of the latter, as far as utilizing available heat producing power is concerned.

**The Melting Points of Iron Carbon Alloys** is an interesting field which has been recently reported upon by Messrs. CARPENTER and KEELING, before the *Iron and Steel Institute*. The temperatures were measured by thermo-electric junctions, calibrated by direct comparison with the nitrogen thermometer up to  $1000^{\circ}$  C., and extrapolated above. Thirty-eight alloys were made by melting Swedish charcoal iron with wood charcoal, and it is believed that the melting points were determined to within  $5^{\circ}$  C. The beginning of solidification was found to be, for pure iron,  $1505^{\circ}$  C.; with carbon 1 per cent,  $1444^{\circ}$ ; carbon 2 per cent,  $1368^{\circ}$ ; carbon 3 per cent,  $1278^{\circ}$ ; carbon 4 per cent,  $1173^{\circ}$ ; saturated at 4.3 per cent,  $1139^{\circ}$ . The results are represented by the equation  $t = 1505 - 54.65 C. - 7.1 C^2$ , wherein C is the percentage of carbon. It will be noted with surprise that while the first one per cent of carbon lowers the

melting point of iron 61°, the fourth per cent lowers it 105°. This method of stating the result is, however, not strictly accurate scientifically, since the effect of equal increments of carbon on a fixed amount of iron should be the basis of comparison, and not upon a regularly decreasing quantity. If the data given by Messrs. Carpenter and Keeling are reliable, however, it must be true that the fourth increment of carbon is more powerful than the first, in lowering the melting point, and our physical chemists have a very stubborn "why?" to overcome. The final part of the paper dealt with the critical points of these alloys, and confirmed in general the outlines of the Roozeboom diagram, which is familiar to all students of the physics of iron and steel.

*Pyrometers Suitable for Metallurgical Work.*—The Iron and Steel Institute gave a half-day, at its recent spring meeting, to the inspection and discussion of various pyrometers. Thirteen different instruments were exhibited, the only new ones being the Zaubitz pyrometer, whose construction was not described, and the Baird and Tatlock pyrometer, which latter has two opposed thermo-junctions. The Le Chatelier and the Nehling are stated to be in wide use in England. In the discussion, Prof. T. Turner, of Birmingham, described a novel means of determining melting points. The substance is placed on a piece of fireclay along with several pieces of metals of higher and lower melting points, the whole is put into a muffle, the gas lit and times taken by a stop-watch. The melting points of the metals are plotted on cross-section paper, as ordinates, with the times at which they melt as abscissæ, and a smooth curve drawn through these. The time at which the unknown substance melted being noted, its melting point is found on the curve. The advantages of this method are that it depends only on having pure metals of known melting points, and that the higher temperatures are not crowded together, but rather drawn apart by the method used. Mr. Gledhill recommended the Siemens water pyrometer, using an

iron ball, as most suitable for determining the temperature of armor plate in a furnace. This is also the experience of a large American steel works, which has tried all other forms of pyrometers.

*Chemical Application of N-Rays.*—The latest kind of radiations which have been examined during recent years—the so-called N-rays—have been found by A. COLSON to be given off during certain chemical reactions and their occurrence can be utilized as a physical criterion for such reactions. His paper is published in *Comptes Rendus* of May 2, and abstracted in *London Electrician*, May 20. The chemical reactions which give rise to N-rays are invariably accompanied by some physical action such as contraction. Some very vivid chemical reactions, like the precipitation of salts, are not accompanied by any evolution of N-rays, so that there is evidently no proportionality between the chemical reaction and the evolution of N-rays. It is just this lack of proportionality which makes the N-rays valuable to the chemist, since he is thus enabled to discover reactions which may be masked by other more evident chemical reactions. A solution of aluminium sulphate mixed with a saturated solution of potassium sulphate at the ordinary temperature gives out neither N-rays nor N'-rays, but if the supersaturation of the alum whose elements are found in the solution is made to cease, N'-rays appear. Similarly, sodium sulphate in a supersaturated solution gives off N'-rays when the supersaturation is stopped by the addition of a crystal and the radiation ceases when the crystals are all deposited. Powdered chrome alum, thrown into cold water, increases the brightness of the calcium sulphide screen, while the violet solution is being formed. But if boiling water is used and the solution is rapid, the emission of N'-rays is such that the luminosity of the sulphide disappears almost completely. Thus the solution of chrome alum leads to the emission of N-ray, while its decomposition by hot water leads to the emission of N'-rays.

## RECENT METALLURGICAL PATENTS.

### MANUFACTURE OF SILICA TUBES.

The manufacture of chemical apparatus from "vitrified quartz" has attracted the interest of various experimenters during recent years, on account of the exceedingly small coefficient of expansion, the high melting point and the very great resistivity of such articles against sudden temperature changes. The manufacture of articles from silica meets, however, with very great difficulties. On account of the exceedingly high temperature required, either the oxyhydrogen flame or the electric arc has been applied, the former, for instance, by Heraeus, who has made chemical apparatus of quartz of various forms or sizes, (*ELECTROCHEMICAL INDUSTRY*, vol. I. pages 366, 586), while experiments made with the electric arc were described by R. S. Hutton in an American Electrochemical Society paper (*ELECTROCHEMICAL INDUSTRY*, vol. I., page 58).

An interesting method of making silica tubes or other hollow articles has now been patented by Elihu Thomson (Patent 761,111, May 31). He also utilizes the heat of the electric arc. At the start of manufacture the ends of two carbon rods of suitable cross-section, forming the electrodes, are in contact. Pulverized quartz is placed around the rods. The electrodes are then slowly removed from each other, drawing a gradually lengthening arc and thereby producing a progressive fusion of the quartz next to the electrode surface. As the arc lengthens, a tube of quartz is formed. When completed, this tube is mounted upon a carbon rod and inserted in the flame of an arc; thereby a fusion and compacting of the exterior surface of the tube is produced so as to render it smooth.

### GOLD.

A combination of electrolysis with the chlorination process for gold extraction from ores is patented by W. E. Greenawalt (761,164, May 31). By electrolysis of salt water chlorine is produced at the anode; it is exhausted from the electrolyzing cell and conveyed into the scrubbing tower, where, coming in contact with water in a state of subdivision a saturated solution of chlorine is obtained, which flows into a storage tank. The barrel, used for leaching, is then charged with ore and solution, and revolved for a short time, say about one hour. During this time much or most of the chlorine has been consumed by satisfying the base elements in the ore. The old solution in the barrel is then displaced by a fresh quantity of new solution under pressure and the barrel is again revolved to extract the precious metals. An illustrated description of the Greenawalt plant at the Wallstreet Mills in Colorado was given in *ELECTROCHEMICAL INDUSTRY*, January, 1904, page 24.

P. Danckwardt (760,429, May 24) patents a filter for extracting valuable metals, such as gold, silver, copper, zinc, etc., from low-grade ores or slimes that cannot be leached in an ordinary tank with a heavy layer of ore, or which require such fine grinding that leaching from a tank becomes an impossibility, and for which the present processes in use, viz., those by decantation of filter-presses or suspended filters, are too expensive. His filter is composed of a series of shells, arranged on successively-lower levels, with inclosed filtering chambers. Pipes connect the bottoms of the shells with the

tops of the next lower shells. Solvent pipes enter the bottom of the shells and suction pipes enter the filtering chambers.

#### NICKEL.

Mond has formerly described the following process for recovering nickel from its ores. The ore is calcined, so as to get it into the condition of an oxide; the oxide is reduced by the action of reducing gases, like water gas; the spongy nickel metal thus obtained is treated with carbonic oxide, producing a compound vapor, mixed with an excess of carbonic oxide and called by Mond "nickel carbon oxide," but now generally known as "nickel carbonyl." This substance can be separated as a liquid, which, on being heated, vaporizes and becomes decomposed, the carbonic oxide being liberated and pure nickel being decomposed as coherent metal.

James Dewar (760,852, May 24) remarks that the nickel carbonyl vapor at ordinary pressures is very unstable, its components becoming rapidly dissociated with explosion on moderate elevation of temperature, so that its production has hitherto been carried on at a moderately low temperature, such as 50° C. Dewar has found that under considerable pressure, ranging from 2 atmospheres to 100 atmospheres, the compound, either as vapor or as liquid, is much more stable, and therefore higher temperatures can be used in its production, whereby the rapidity of process of manufacture is greatly increased. Thus for the gasification of the nickel a temperature of 100° C., with a pressure of 15 atmospheres is suitable, or a temperature of 180° C., with a pressure of 80 atmospheres. The spongy nickel obtained by the reduction by means of water gas, if treated at the temperature and pressure mentioned, combines rapidly with the carbonic oxide, producing vapor of nickel carbonyl. This vapor, with the excess of carbonic oxide in which it is diffused while still under pressure, on being passed through tubes of a higher temperature, becomes dissociated depositing metallic nickel, while the separate and diluent carbonic oxide can be returned to act on the fresh charges of spongy nickel.

#### ALUMINIUM.

C. Ellis (760,783, May 24) patents a flux for soldering aluminium, "consisting of a heavy metal salt whose heat of formation is less than the corresponding salt of aluminium, a saline body whose heat of formation is greater than the corresponding salt of aluminium and an organic body." As an example is given a mixture of 10 parts of silver bromide, 9 parts of sodium fluoride and 25 parts of melted wax. The mixture is stirred until the solidifying point is nearly reached, when the plastic mass may be moulded into the form of sticks or pencils. If the mixture is to be applied in paste form, a solvent may be added, such as turpentine, alcohol or paraffin oil.

#### ROASTING FURNACES.

Franz Meyer (761,691, June 7) patents a muffle-roasting-furnace which comprises a series of roasting chambers. Each is formed as a separate unitary structure, effectively braced and anchored against the disrupting effects of expansion by means of an enclosing metallic shell, lined with refractory material. A heating furnace is common to the series of roasting chambers. Suitable flue connections are provided, with expansion joints between the successive chambers of the series, and means for preheating the air for oxidizing the sulphur in the ore.

C. C. Wilson (760,941, May 24) patents a revolvable cylindrical ore-roasting and automatic ore-feeding and rabbling furnace. From the walls of the revolvable ore-roasting chamber project longitudinal shelves constructed to cause the ore to drop from shelf to shelf and to move inwardly and outwardly on the opposite side of each shelf.

A. A. Bean (761,646, June 7) patents a revolving cylindrical return-flue furnace. It contains three horizontal concentric cylinders, providing two compartments with annular cross-section and one with circular cross-section. The combustion and smoke chambers are connected to the opposite ends of the

outer and inner compartments. The ore is fed into, conveyed through, and discharged from the middle compartments, while means are provided for introducing air and steam into the middle compartment, and for rotating it.

W. H. Smyth (761,049 and 761,050, May 24) patents an ore-roasting furnace whereby the rabble-carrying and operating mechanism is carried entirely outside of the furnace and thus is protected from heat and destructive gases of the furnace. In his multiple-hearth furnace he uses a plurality of superimposed slotted-hearth furnaces, rabbles adapted to travel above the hearths, to stir the ore thereon. Travelling bands effect the travel of the rabbles or stirrers, the parallel stretches of which travel in the same vertical plane. The slots are closed by flexible overlapping plates.

#### MELTING FURNACE.

J. Southern (760,495, May 24) patents a furnace for melting metals. The heavy thick front wall of the furnace is built of brick and provided with apertures or combustion-chambers which extend from front to rear. The middle portion of these chambers is enlarged and their further ends branch into a greater number of openings to discharge heat into the melting chamber.

#### MISCELLANEOUS METALLURGICAL APPARATUS AND APPLIANCES.

J. Kennedy (760,873, May 24) patents details of construction of hot-blast valves in which the valve seat is gripped between two sections of the valve casing. The patent refers especially to the methods of gripping and releasing the valve-seat.

W. H. Hume (762,721, June 14) patents details of construction of reversing valves, used to regulate and control both the flow of gas and air to a Siemens regenerative furnace, and the discharge of the spent gas into the stack. He endeavors to eliminate any feature of mechanical nature. For this purpose he provides a chamber with two separate open compartments upon its floor, a passage from the chamber to the furnace, an inlet-passage for gas or air extending down into one of the open compartments, an exit passage for spent gas extending down into the other open compartment, and water in the two separate open compartments for alternate action upon the open ends of the inlet and exit passages to regulate and control the flow of gas and air and the discharge of spent gas.

A. Kurzwernhart (760,633, May 24) endeavors to prevent the loss of gas on reversing the controlling valve in a Siemens regenerative furnace. Before the reversing operation, the gas contained in the regenerative chamber and in the passages connected therewith is forced into the furnace by air which, after the gas has been cut off in a known manner, is introduced through a lateral opening.

N. J. Norman (761,900, June 7) patents a welding flux for welding two pieces of copper or metals. It is formed of the following ingredients in pulverized form; 4 parts sal-ammoniac, 3 parts saltpeter, 3 parts sal-soda, 4 parts yellow prussiate potash, 5 parts borax and 3 parts pulverized glass.

The casting of slag or cinder from blast furnaces into the form of brick or building block has proven a useful and remunerative way of disposing of this by-product. E. A. Uehling (760,825, May 24) describes a device in which the moulding of the brick and its annealing is carried out at one and the same time. The bricks are annealed by means of their own latent heat and the method is claimed to be rapid and economical.

H. L. Gantt (762,301, June 14) describes a forge furnace which affords a high temperature, and in which the tools or other articles to be heated need not be placed in contact with the fuel, but in a specially provided chamber.

M. Slotkin (762,005, June 7) provides a foot-power mechanism for driving the fan of small forges, so that both hands are free for holding and manipulating the article in the forge.

W. J. Newton, R. Diggle and G. Watson (763,199, June 21) patent details of construction of dust arresters in order to provide an automatic and effective means for arresting or pre-



venting the escape of dust or the like from refuse burners or other furnaces and flues, the arrangement being made that the accumulated matter may be removed without interfering with the furnace draft.

F. W. Shupert, J. Wormald and H. L. Shupert (761,418, May 31) patent details of construction of the arches in the fire-boxes of locomotive engines. They use a body portion of baked fire clay with an internal strengthening structure composed of iron rods with asbestos covers.

## Correspondence.

### THE CHEMICAL ENGINEER.

TO THE EDITOR OF ELECTROCHEMICAL INDUSTRY:

Sir—Considering the source from which it emanated, and the ripeness of the time for the agitation, it is not surprising that the paper delivered by Mr. J. B. F. Herreshoff, before the American Chemical Society on the "chemical engineer," (ELECTROCHEMICAL INDUSTRY, May, 1904) has attracted wide notice by abstraction, and excited much discussion at the time of its presentation.

The value of an engineering training, supplementary to the usual technical equipment of a chemical graduate, is obvious, and the matter at once resolves itself into a consideration of the most advantageous course for a young man to pursue in order to fit himself for tackling industrial chemical problems. The figures quoted in the early part of Mr. Herreshoff's paper plainly show the enormous proportions our chemical industry has attained, and it is farther true that the field wherein these operations are carried on contains a more varied and at the same time somewhat closely allied series of processes than those underlying any other single branch of commercial activity.

It would seem, therefore, as though the industry had reached that stage where our present educational system were inadequate to supply the demands of its vigorous advance, and the query very naturally arises whether the field is not large enough to accommodate two specifically trained classes of chemists, in addition to requiring on occasions the services of an engineer for problems clearly within his province.

In any event the trained analyst is a necessity. It is true that the educated "wash boy" becomes in time an economical and valuable member of the laboratory community, but he has his limitations, and it is doubtful in my mind whether his growing presence to the exclusion of college-trained men among the staff of an industrial laboratory is a wise policy.

The chemists which our colleges are yearly turning out, are more fitted for the analytical than for any other department of a chemical manufacturing establishment, and in many cases it is only too apparent that a recent graduate is incapable to manipulate with rapidity and accuracy required in a "works" laboratory.

Considering that nearly 75 per cent of the time spent upon chemical subjects in our university chemical courses is devoted to analytical work, and that this is scarcely adequate to produce a first class analyst, one of two conclusions is inevitable; that, first, a young man electing to connect himself with the manufacturing end of the chemical industry must be prepared to gain the necessary preliminary training after leaving college, or, secondly, that our universities must provide a course with the object of inculcating in the student the principles of chemical economics.

I am quite sure that it would puzzle the heads of many chemical departments to outline the daily routine for such a course, as on a number of occasions I have had an opportunity of remarking how completely out of touch the average chemical instructor is with the particulars of large scale operations. This condition is possibly in part due to the secrecy maintained by the majority of the manufacturers in this

country. It is questionable, however, whether the various chemical plants contain valuable original processes or whether, as some one else has suggested, their dilapidated and inefficient state urges an exclusion of visitors.

However, be that as it may, it is a digression from the object of these lines, viz., to offer a few suggestions as to an alternate course in chemistry in our technical schools. It must be admitted that by virtue of the inherent differences between demonstrating a process and the operating of a plant where labor, location and cost of materials, etc., have such a direct bearing on the method followed, it is a different problem to arrange a course of work sufficiently comprehensive to be of material advantage to the student.

A great part of the work in quantitative analysis might be eliminated from the present course without working injury to the training of the future chemical engineer.

This change would place at our disposal say ten hours per week to be devoted to studies of a strictly technical bearing.

I used above the phrase, chemical economics, and if I do not mistake Mr. Herreshoff's idea this describes perhaps more accurately than "chemical engineering" the branch of the industry for which his plea was made. Here certainly is one phase of the problem of chemical manufacturing of which the young graduate is comparatively ignorant.

He naturally realizes that cheapness of production consistent with quality is the good to be sought, but his chemical education has not laid stress on certain economical principles governing the proper procedure in several operations common to many processes, *e. g.*, teaching absorption of gases by liquids, tower packing, mist condensation, etc. A theoretical consideration of such points would be of great value in preparing for an industrial career.

Next in importance I would rank a study of the economical significance of physico-chemical phenomena. While physical chemistry is at present a prominent factor in the usual chemical curriculum, it is doubtful whether the student has received a training that permits of practical application of the principles absorbed.

Electrochemical possibilities should by no means be neglected, and in this connection an opportunity should be taken advantage of to familiarize the student with the control of the electric current, and with electrical apparatus.

The transmission of power and the handling of material are of immense importance in a chemical factory, yet I venture to assert that the newly graduated chemist is quite unfamiliar with the various mechanical devices for these purposes, and would be therefore greatly handicapped in designing a simple plant, even were the chemistry involved perfectly clear to him.

Steam, the *sine qua non* of a chemical plant, is, so far as its economical and efficient use is concerned, a new friend to the chemical graduate.

One further subject, the choice of materials of construction, offers itself to most profitable and careful study, which now is altogether too lightly touched upon in the college courses.

A well-conducted training along these lines I have very briefly enumerated. I am convinced would save a man many months, and make a sound foundation from which to evolve the type of industrial chemist of which Mr. Herreshoff declared the need.

W. MURRAY SANDERS.

Ioja, Kansas.

## Current Notes.

REVOLUTIONARY CHARACTER OF ELECTROCHEMISTRY.—In commenting on Dr. J. W. Richards' last presidential address before the American Electrochemical Society, the *Engineering and Mining Journal* says, "The production of a half-ton of silicon at a moment when that element is listed as a rare chem-

ical at so many dollars per ounce, does indeed happily illustrate the revolutionary character of electrochemistry. The chemist is to the metallurgist what the prospector is to the mining engineer; he adventures into unknown territory and wins new country for exploitation; only in his case the greater scientific acumen is apt to be with the pioneer rather than the exploiter."

**AMERICAN ELECTROCHEMICAL SOCIETY.**—At the meeting of the Board of Directors, held on June 7, the following gentlemen were elected to membership: George Breed, Philadelphia, Pa.; Alexander Lodyguine, Staten Island, N. Y.; Charles Jackson, Guadalajara, Mexico. The dates of the St. Louis meeting were fixed for the 13th, 15th and 16th of September. On the 13th and 15th, joint sessions will be held with Sec. C. (Electrochemistry) of the Fifth International Electrical Congress, and on the 16th a joint session will be held with the Bunsen and Faraday Societies. Sessions will only be held in the morning. No session is being arranged for the 14th, as it is thought by officers of Sec. C. that if an independent meeting is set for the 16th, rather than the 14th, that the section may be through with its work by that time and be able to attend our session. Our members can in this way have the opportunity of attending the congress. At the next meeting of the Board of Directors, to be held on July 1, the names of the following gentlemen will come up for election to membership: H. E. Eggers, Santa Cruz, Cal.; George C. Hitchcock, Claremont, Cal.; F. L. Wadsworth, Morgantown, W. Va.; William C. L. Eglin, Philadelphia, Pa.; E. Humblot, San Francisco, Cal.; P. McN. Bennie, Niagara Falls N. Y.; J. W. Best, Denver, Col.

**NEW USE FOR ALUMINIUM.**—According to *La Métallurgie*, at a recent meeting of the "Société d'Encouragement pour l'Industrie Nationale," a paper was read on the substitution of aluminium for wood in the machinery of spinning mills. In the textile industries—spinning, dyeing, and silk weaving, among others—a wooden bobbin is generally used. This is cheap and easily worked, but it has many drawbacks. Being very hygrometric, it suffers from variations of temperature; this accounts for the fact that in spinning factories where the atmosphere is full of humidity the bobbins revolve irregularly, causing jerks which slacken the speed and occasion the threads to break. The result is waste of stuff and loss of time in joining the threads again. It has been proposed to substitute aluminium for wood. Bobbins made of this metal revolve in any temperature and any degree of humidity; their relative lightness (five aluminium bobbins weigh no more than two wooden ones) allows the machines carrying them to move more quickly, or an equal speed may be obtained at less expense of power; finally, the smaller volume of the bobbins diminishes the cost of transport. It was stated that several firms had adopted the use of aluminium bobbins and had found that they possessed many advantages.

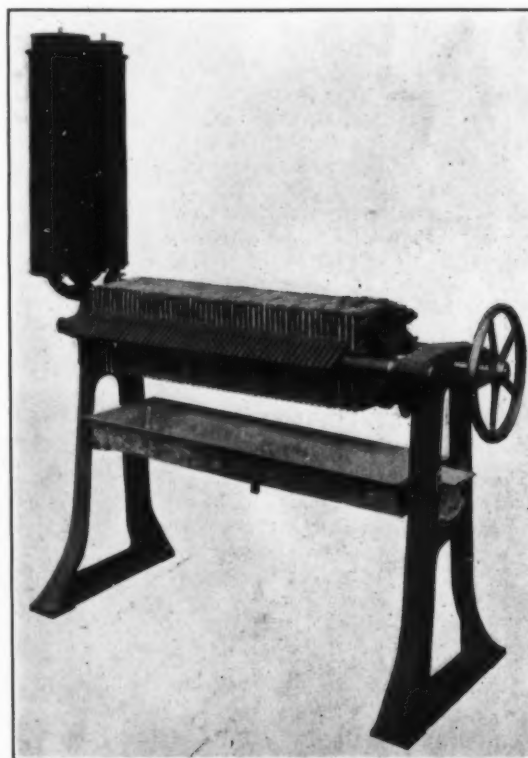
**NEW METHOD OF COLOR PHOTOGRAPHY.**—Auguste and Louis Lumière describe a new method of photographing in natural colors in *Comptes Rendus*, May 30, an abstract being given in the *London Electrician* of June 17. The method is somewhat similar to Joly's method, except that colored starch grains are substituted for tinted gelatine lines. From the starch of potatoes, the grains having a diameter of 15 to 20 microns are separated out. They are divided into three lots, which are colored orange-red, green and violet, respectively. After thorough drying, the colored powders thus obtained are evenly spread on a glass plate covered with a layer of isinglass. With care, one succeeds in spreading a very uniform layer only 1 grain in thickness. Then any interstices are closed up by means of a black powder, such as powdered wood charcoal. One thus obtains a color in which every square millimeter contains 2,000 or 3,000 elementary screens of the primary colors. The surface is then covered with a layer of thin transparent varnish having an index of refraction equal to that of the

grains of starch, and, lastly, an isochromatic film of gelatine-bromide of silver is applied. The sensitive plate thus obtained is exposed in a camera in the ordinary way, except that exposure is made through the glass slide. A pure red surface produces a blackening of the film behind every red particle, leaving it unaffected behind the others. On developing and fixing, such a plate will, therefore, show the complimentary color of the original. To obtain the correct color, the authors dissolve away the reduced silver and develop the unexposed chloride. They thus obtain a transparency in the natural color without much more trouble than that of taking an ordinary photograph.

#### ELECTROLYTIC PRODUCTION OF HYDROGEN AND OXYGEN.

We have repeatedly described in our columns commercial apparatus for the production of oxygen and hydrogen gases by electrolysis of water; a comprehensive summary of methods for preparing and compressing these gases for experimental work was given in the paper by R. S. Hutton and A. E. Petavel in our April issue, 1904, page 139.

Hydrogen is at present mainly used for inflating military balloons, for autogenous welding and lead burning. For the



ELECTROLYZER FOR MAKING OXYGEN AND HYDROGEN.

latter purpose the oxy-hydrogen flame is also extensively used especially in connection with installing storage batteries, by various European storage battery manufacturers. As far as we know, the electrolytic production of hydrogen and oxygen for such purposes, has not yet found application in this country.

A new apparatus for making hydrogen and oxygen by electrolysis has recently been placed on the market by the Oerlikon Company in Zurich, Switzerland. The apparatus is made in various sizes, consuming up to 30 hp. while the voltage used may be up to 250. The apparatus contains a series of successive cells, the electrodes being brass plates. In its general con-

struction the apparatus is very similar to a filter-press. This will be seen from the adjoining illustration.

The different plates are insulated from each other by means of diaphragms which at the same time assure perfect tightness of the cells. The gases formed at the surface of the electrodes escape through holes in the plates. These holes communicate with two longitudinal canals which conduct the gases to separators in which the gas is separated from the liquid, the latter being conducted back to the cells through a single conduit. A continuous circulation of the liquid is produced by the development of gases due to the passage of the current.

The electrolyte consists of a 10 per cent solution of potassium carbonate. The design of the apparatus permits to obtain the gases under constant pressure, the value of which may be equivalent to the pressure of a water column of  $2\frac{1}{2}$  meters height. On account of the simplicity of construction, it is possible to clean the apparatus rapidly. If it is in continuous operation, it becomes necessary to clean it at intervals of about eight weeks. It is, of course, always necessary to add distilled water to the solution, to make up for the water decomposed by the current.

This apparatus decomposes 134 grams of water per kw-hour, and produces 168 liters of hydrogen and 84 liters of oxygen. At elevated temperatures, the efficiency is increased by 8 per cent.

The purity of the electrolytic oxygen is in the average 97 per cent, the 3 per cent impurities being hydrogen and some carbon monoxide. The electrolytic hydrogen on the other hand contains only one per cent of oxygen. By means of special and very simple devices, it is claimed, that it is possible to obtain the gases in a condition of perfect purity.

In the cold the electrolyzer requires 2.7 volts per cell, which is reduced at elevated temperatures to 2.3 volts. When the apparatus is started, the temperature increases for about eight hours; after this interval the temperature becomes stationary, being about  $60^{\circ}\text{C}$ .

On the basis of a price of 1.2 cents per kw-hour of electrical energy, the cubic meter of oxygen costs 14.1 cents, and the cubic meter of hydrogen 7.2 cents.

### ST. LOUIS EXPOSITION.

#### INTERNATIONAL ACHESON GRAPHITE COMPANY.

The exhibits of the International Acheson Graphite Co., are placed near the main entrance of the Electricity Building. They comprise miniature electric furnaces, illustrating the processes



EXHIBIT OF INTERNATIONAL ACHESON GRAPHITE CO.

of E. G. Acheson for manufacturing artificial graphite from anthracite coal, as worked on a large scale at the plant of the company in Niagara Falls (see description *ELECTROCHEMICAL INDUSTRY*, October, 1902, page 52). The exhibits comprise the different grades of graphite and various forms and sizes

of electrodes, showing the great ease of machining Acheson graphite so that the graphite articles may be assembled in any desired form. For electric furnace work, when an electrode has been consumed, it is only necessary to join a new one to the end of the old one, and feed into the furnace one after the other without interrupting the operation. Other exhibits illustrate the use of Acheson graphite for the manufacture of paint, dry batteries, stove polish, motor generator brushes, etc. Special attention is given to the use of this form of pigment for high-grade protective coatings on structural iron and steel, for instance for bridges.

#### HALL'S PLATING WORKS.

An attractive operating exhibit is the Hall model electroplating establishment in the West doorway of the Electricity Building. The various steps in the processes of gold and sil-



HALL'S ELECTROPLATING EXHIBIT.

ver plating are shown, such as cleaning the metal surface, depositing the electrolytic coating, cleaning and polishing. Electroplated leaves, fruit and flowers are specially attractive.

#### HEADQUARTERS OF ELECTROCHEMICAL INDUSTRY.

The headquarters of *ELECTROCHEMICAL INDUSTRY* will be in conjunction with the offices and exhibits of the McGraw Publishing Co. The space is at the head of the main aisle



BOOTH OF MCGRAW PUBLISHING COMPANY.

(section one) in the Electricity Building. The booth is elegantly and comfortably furnished for the reception of visitors. A library is provided with a very complete collection of engineering books, including important works on electrical, mechanical, mining, metallurgical and chemical subjects. Com-



plete files of the following publications are available for inspection and reference: Electrical World and Engineer, Street Railway Journal, Engineering Record, American Electrician, ELECTROCHEMICAL INDUSTRY, American Street Railway Investments, Electrical Railway List and Buyers' Manual, Central Station List and Manual of Electric Lighting. Facilities are provided for receiving mail in care of the McGraw Publishing Company, and a register is kept in which it is intended to have a complete record of all those interested in any branch of electrical engineering who go to the Exposition.

#### INTERNATIONAL ELECTRICAL CONGRESS.

For the International Electrical Congress, to be held in connection with the Exposition, the following foreign governments have appointed delegates: Switzerland, Prof. Ferdinand Weber, Prof. Francois Louis Schule; Norway and Sweden, Prof. S. Arrhenius; India, Mr. J. C. Shields; Mexico, Mr. Rafael R. Arizpe.

The appointments from Great Britain, France, Germany, Austria-Hungary, United States, Belgium, Italy, Denmark, Spain, Portugal, Australia, Japan, China, Brazil, Chili and Peru have not yet been made. It is stated that appointments are being made.

#### A DEOXIDIZER FOR THE USE OF STEEL MANUFACTURERS AND FOUNDERS.

One of the great difficulties which steel and iron manufacturers and founders, as well as copper founders, have to contend with, is the occurrence of blow holes, flaws and "pipes" in the ingots and castings. The cause of these flaws is well known; they are due to oxygen. In steel and iron making and casting the oxygen combines, unless it is prevented from doing so, with the carbon which is always present, to form carbonic acid, and this combining action takes place rather slowly and even during the solidification of the metal, so that blow-holes are always liable to be formed. In the case of copper the trouble is that cuprous oxide dissolves in fused copper.

The remedy is, of course, to apply some deoxidizing agent. In the case of copper, the practice is now to add a small amount of silicon-copper; the silicon takes away the oxygen from the cuprous oxide and forms silica (ELECTROCHEMICAL INDUSTRY, March, 1904, page 121). In the case of iron and steel castings, aluminium has been tried since it has a very great chemical affinity for oxygen, as shown by its extremely high oxidation heat. But a difficulty arises in this case on account of the lightness of aluminium which tends to flow on the surface of the molten metal; an interesting method of overcoming this difficulty, described in our November issue, 1903, page 533, is by the use of anti-piping thermit.

A method of very general applicability for removing the blow-holes and produce sound ingots and castings, is to add to the steel or iron an alloy of metals which will combine with all the occluded gases—an alloy, consisting of several metals, such as aluminium and manganese having a greater chemical affinity for oxygen than the metals to be cast, and one or more electronegative non-metallic elements or metalloids, such as silicon or boron. By taking up the oxygen from the castings, the elements of this alloy are converted into single, double or multiple silicates, borates, etc., which produce a readily fusible slag. This slag is very quickly formed and rises in the form of globules upwardly through the liquid and much heavier material of the casting and renders the latter pure and free from blow-holes.

On this general principle is based the preparation of an alloy which is made by Messrs. George G. Blackwell, Sons & Co., Ltd., of Liverpool, England, under the name of S. A. M. Alloy. It is added to the molten steel or iron in such proportions that practically only a trace of the constituents of the same or say less than one-tenth of one per cent, remain in the finished casting, it being, of course, understood

that the iron added by the alloy is in such proportion that more or less of the same is not oxidized and remains in the finished casting, while the remaining elements of the alloy are practically completely oxidized and form a readily fusible slag. The actual quantity of the alloy added to the molten iron or steel will, of course, depend upon the amount of oxygen found to be contained in the iron or steel. It will, therefore, depend on the special conditions in each case, and experiments should be made in which the quantity of the S. A. M. Alloy added is varied from one-half per cent to 1½ per cent, until the best results are obtained. Under ordinary conditions from one-half to three-quarter per cent of the alloy will be found sufficient in the treatment of basic and other steel.

It is naturally of great importance that no impurities should be introduced into the bath by this alloy. This is fully taken into consideration in the preparation of the S. A. M. alloy. Outside the special elements, it contains about 1.10 per cent of carbon, 0.05 per cent of phosphorous and 0.01 per cent of sulphur. The method of using this alloy is very simple. In open hearth steel the rule is to add the alloy red-hot, broken up, to the stream of molten metal, as it is being tapped from the furnace into the ladle. It may also be added direct into the ladle. It should not be added through the slag, but to the clean metal. In making crucible steel, the rule is to break the alloy into small pieces, heat to red heat, mop off slag, and stir into the pot just before teeming.

While the alloy is of general applicability, it has been found to be especially useful in the manufacture of special high-class, products, like armor plates, gun-forgings, boiler tubes, etc. For marine boilers it is recommended to make the tubes from extra soft chrome nickel steel, practically free from manganese, and "kill" with S. A. M. alloy. Such a tube withstands the action of fire and steam to a remarkable extent. It is made by Messrs. George G. Blackwell, Sons & Co., Ltd., from their refined ferro-chrome, which contains, under one per cent of carbon or from their chrome-nickel alloy.

#### PERSONAL.

The Committee of Science and Arts of the Franklin Institute has decided to confer the Elliott-Cresson medal to Dr. HANS GOLDSCHMIDT in Essen-Ruhr, Germany, in recognition of his distinguished work in aluminothermics.

JUBILEE.—In view of the approaching fortieth anniversary of Dr. Charles F. Chandler's appointment as professor of chemistry at the foundation of the School of Mines of Columbia College, the alumni association of the University is raising funds to present his portrait to the university. Prof. Chandler is not only well known to all old students of Columbia, but is held in the highest esteem by chemists all over the world. He was the first American elected president of the Society of Chemical Industry. For the sake of electrochemistry he has done very enthusiastic and important pioneer work.

At the recent commencement exercises of Lafayette College, Mr. WILLIAM H. NICHOLS, president of the General Chemical Co., and of the Nichols Chemical Co., received the honorary degree of LL.D. Dr. Nichols has also been nominated by the council of the Society of Chemical Industry, to succeed Prof. Ramsay as president. For the second time in the history of this Society an American will be elected its president. The first to enjoy this honor was Dr. Charles F. Chandler, of Columbia University, as the representative of chemical science in America; the second one is Dr. W. H. Nichols, representing American chemical industries.

#### INDUSTRIAL NOTES

CAUSTIC SODA.—We have received from Mr. Max Mauran, superintendent of the Castner Electrolytic Alkali Co., Niagara Falls, N. Y., two sample bottles of their electrolytic

caustic soda. One contains pieces of caustic, broken out of a drum, showing the crystalline structure of the caustic very clearly. The samples in the other bottle are made up in form of moulded sticks. The company puts the caustic up in this form for laboratory use as it is a little more convenient in this way. Tests of the caustic soda concerning purity have shown that it is over 99.5 per cent NaOH.

**THERMIT.**—We have received from the Goldschmidt Thermit Co. a small bottle containing a portion of the first thermit made in the United States from United States materials. The factory of this company has recently been installed in New York by Dr. O. Weil, chief chemist of the thermit department of Messrs. Th. Goldschmidt & Co. in Essen.

**RUTILE.**—We have received from the American Rutile Company, Washington, D. C., samples of their rutile ores from their Virginia mines, and also a sample of their powdered rutile. While rutile has various applications, there is now a steadily growing demand for it on account of the increasing importance of ferrotitanium in the iron and steel industries. Concerning the effects of ferro-titanium we may refer to an article, vol. I., page 525, of this journal.

The "Metallurgical Company of America" has recently been incorporated under the laws of the State of New Jersey, with a capital of one million dollars, for the purpose of doing a general metallurgical business. The officers of the company are Walter Merton, president; Dr. F. Meyer, treasurer; L. Seeger, secretary. The directors of the company are B. Hochschild, J. Langeloth, Louis J. Magee, Walter Merton, F. Meyer.

Among the sales made by CROCKER-WHEELER COMPANY during the past week is that of electrical machinery to the value of about \$30,000 to the Barbour Flax Spinning Co., Paterson, N. J. The equipment includes a 600-kw. standard direct-current, 250-volt generator, and motors, with ratings from 5 to 100 hp., aggregating 515 hp. Also for their plant in Baltimore, the W. & J. Knox Net & Twine Co., they have bought a 100-kw. generator and 75 hp. in motors. The United States Naval Academy, Annapolis, has just purchased two 250-kw. Crocker-Wheeler generators for a two-unit, three-wire lighting system; and the J. B. Williams Company, of Glastonbury, Conn., a 150-kw. engine type generator. Armour & Co., Chicago, who already use C.-W. motors to the amount of about 7,000 hp., have placed an order for three more machines aggregating 110 hp. Twenty-eight motors, of the same make, with a combined power of 253 hp., have just been purchased by the Traitle Marble Co., Ravenswood, L. I.

Since the equipment of factories with electric motors for individual and group drive of machine tools has become an extensive department of the business of the Crocker-Wheeler Company, this company is now going a step further. It has retained the well-known firm of Dodge & Day, of Philadelphia, Pa., and places the services of this firm at the disposal of its customers. The advice and recommendations about which customers of the Crocker-Wheeler Co. may consult this firm need not be confined to electrical details, but may include all problems of shop equipment and management.

**MASSENA WATER POWER.**—The establishment of the power plant of the St. Lawrence Power Co., at Massena, New York, seems to have had a great effect on the growth of that town, which but a short time ago was simply a summer resort. It is stated that in the last year and a half the population of Massena has been doubled, it now being about 7,000, and that in spite of the active building operations there are no houses available for renting. The St. Lawrence Power Co. is now supplying power to the Pittsburg Reduction Co., The Indestructible Fibre Co., The Massena Mineral Fibre Co., The Massena Pulp and Paper Co., The Massena Sash and Door Co., and The Massena Machine Works, as well as for lighting the town. The present development amounts to 35,000 hp.

## DIGEST OF U. S. PATENTS

PRIOR TO JULY, 1902.

Compiled by Byrnes & Townsend,  
Patent Lawyers,

National Union Building, Washington, D. C.

### THE PRODUCTION OF SODIUM FROM MOLTEN ELECTROLYTES.

296,357. April 8, 1884, Augustus J. Rogers, Milwaukee, Wis.

Electrolyzes molten chlorides, bromides, iodides, fluorides, sulphides, oxides, etc., of potassium, sodium, calcium, barium, strontium, magnesium, aluminium, boron, silicon, phosphorus, etc. May use a mixture of compounds to increase the conductivity or fusibility of the electrolyte, *e. g.*, adds calcium chloride to potassium or sodium chloride, in equi-molecular amount, thereby lowering the fusing point from 730° to 500°. Similarly, adds potassium and ammonium chlorides to magnesium chloride. The apparatus comprises a rectangular cell of clay set in masonry, with an ordinary fireclay diaphragm which extends nearly to the bottom. The electrodes are carbon plates, having terminals which extend through the sides or top of the cell, and are protected from the electrolyte by clay tubes. The cell has a tight cover which seats on the diaphragm and has feed-openings and two goose-necks, one leading to a coil condenser for the electrolyzed sodium, and the other to a lime chamber. The cover also has an exhaust pipe for removing the air from the cell before starting. An atmosphere of hydrogen is maintained in the upper part of the cathode compartment to prevent oxidation of the sodium. The molten salt is supplied to the cell from a separate clay or iron melting pot, which has a valved outlet leading into the bottom of the cell beneath the diaphragm. The melting pot has a float-feed salt reservoir and a safety valve. The sodium condenser has outlets into two receptacles containing coal-oil.

452,030. May 12, 1891, Hamilton Y. Castner, London, England.

Electrolyzes molten caustic soda or potash, or a mixture of both, at the lowest practicable temperature, say 20° C. above their melting point, to prevent recombination of the ions and volatilization of the metal. The cell is a circular iron vessel having a central extension from its bottom through which passes the cylindrical carbon cathode. The joint between the bottom cell extension and the cathode is filled with a solidified sleeve of caustic, the extension being exposed to the air to keep it cool. The cathode extends up into the cell and is surrounded by a tubular anode of a metal which will resist oxidation. A tubular iron receptacle opens into the electrolyte directly above the cathode, and has an iron wire gauze cylinder, which extends down between the cathode and anode. The electrolyzed metal rises into the receptacle and is removed by a perforated spoon or skimmer. A cell for holding 250 pounds of electrolyte employs a cathode four inches in diameter. The electrolyte may be maintained in a molten condition by the current. The preferred temperature for caustic is specified as 310° C.

464,006. December 1, 1891, Ludwig Grabau, Hanover, Germany.

Electrolyzes molten alkali chlorides in a vessel having a cover through which pass the carbon rod anodes, arranged in a circle. The vessel has a lateral chlorine outlet at the top. A bell of porcelain, with a double wall which opens at the top, depends into the electrolyte. An iron tube containing a boring tool passes down through the top of this bell and serves as the cathode, having a wire extension with a cross-piece at its lower end. A lateral outlet for the sodium leads from the iron tube into a condensing vessel which is filled with hydrogen or nitrogen and dips into petroleum.

(To be continued.)

